

**Description****Phosphor, and Light Emitting Device and Lighting System Using the Same, and Image Display Unit****Technical Field**

The present invention relates to a high-efficiency light emitting device obtained by combining a light emitter which emits light in the region from near-ultraviolet light to visible light and a phosphor which absorbs this light and emits visible light having a longer wavelength, and the phosphor itself.

**Background Art**

White light indispensable for displays and lighting is generally obtained by combining blue, green and red light emissions according to an addition mixing principle of light. In the displays, in order to efficiently reproduce colors in a wide range on chromaticity coordinates, it is necessary that blue, green and red phosphors have as high emission intensity as possible and good color purity. In general lighting, it becomes necessary that they have high emission efficiency, and that the color of an object irradiated looks like when it is irradiated with natural light, namely, that so-called color rendering properties are high, depending on some applications.

In a fluorescent lamp which is typical lighting, an ultraviolet ray having a wavelength of 254 nm caused by discharge of mercury is mainly used as an excitation source, and three kinds of phosphors which emit lights of 450nm, 540nm and 610 nm highly sensitive for human eyes are mixed to use, thereby realizing light emission having high color rendering properties. However, when the wavelength of excitation light is in the region from near-ultraviolet light to visible light, no phosphor having high emission efficiency has been developed under the present situation. In particular, to the excitation light in this wavelength range, emission efficiency of the red phosphor is low compared to that of the blue and green phosphors, so that a red phosphor having excellent performance has been desired. When any two or three lights of the above-mentioned 450nm, 540nm and 610 nm are obtained from one phosphor, a blending process is simplified compared to mixing of three kinds of phosphors, and stability of performance is expected. However, it had not been realized.

Various phosphors which emit blue, green and red lights in combination with a light source of light emission in the region from near-ultraviolet light to visible light are exemplified in patent document 1. Of these, an alkali earth metal silicate phosphor is described to emit light in a blue color and a red color. Further, in patent document 2, it is described that a (Ba,Ca,Sr,Mg)-Si-O system activated by Eu<sup>2+</sup>

emits light at 505 nm in the case of only Ba and Ca, and that emission wavelength shifts to 580 nm when Sr is added. In non-patent document 1, there is a report about  $(\text{Ba}, \text{Ca}, \text{Sr})_3\text{MgSi}_2\text{O}_8:\text{Eu}, \text{Mn}$ . Further, in non-patent document 2, it is described that  $\text{Ba}_3\text{MgSi}_2\text{O}_8:\text{Eu}, \text{Mn}$  has emission peaks at 442 nm, 505 nm and 620 nm, and that its crystal structure is merwinite.

[Patent Document 1]

JP-T-2004-505470 (the term JP-T as used herein means a published Japanese translation of a PCT patent application)

[Patent Document 2]

JP-T-2004-501512

[Non-Patent Document 1]

*J. Electrochem. Soc.*, Vol. 115, No. 7, 733-738 (1968)

[Non-Patent Document 2]

*Appl. Phys. Lett.*, Vol. 84, No. 15, 2931-2933 (2004)

#### Disclosure of the Invention

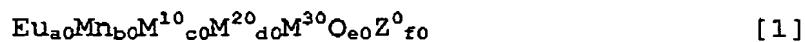
An object of the invention is to develop a high-efficiency red light emitting phosphor and white phosphor for using in a display or lighting which high-efficiently emits light in combination with a light source which emits light in the region from near-ultraviolet light to visible light.

In order to solve the above-mentioned problem, the present inventors have made intensive studies. As a result,

it has been found that an alkali earth silicate phosphor having a novel composition and a specified crystal structure high-efficiently emits red or white light to excitation light in the region from near-ultraviolet light to visible light, thus completing the present invention.

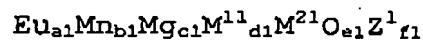
Specifically, the present inventors have found a Ba- and Ca-containing  $M_2SiO_4$  type silicate activated by Eu and Mn, thus arriving at the present invention. In particular, the red phosphor of the present invention has a wavelength of emission peak within the range of 590 nm to 620 nm, so that it is characterized by reddish emission which feels bright.

That is to say, a first gist of the present invention is a phosphor comprising a crystal phase having a chemical composition of the following formula [1], [2] or [3], and a second gist is a light emitting device comprising a first light emitter which emits light of 350 nm to 430 nm and a second light emitter which emits visible light by irradiation of light from the first light emitter, wherein the above-mentioned second light emitter is a phosphor comprising a crystal phase having a chemical composition of the following formula [1], [2] or [3]:



wherein  $M^{10}$  is a divalent element containing 85 mol% or more

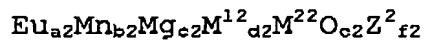
of at least one element selected from the group consisting of Ba, Ca and Sr, in which the ratio (molar ratio) of Ca to the sum of Ba and Ca is from 0.1 to 0.9; M<sup>20</sup> represents at least one element selected from the group consisting of a monovalent, trivalent and pentavalent elements; M<sup>30</sup> represents a group of tetravalent elements containing Si and Ge in a total amount of 90 mol% or more; Z<sup>0</sup> is at least one element selected from the group consisting of a minus monovalent and minus divalent elements, H and N; and a0 is a number satisfying  $0.001 \leq a_0 \leq 0.6$ , b0 is a number satisfying  $0 < b_0 \leq 0.7$ , c0 and d0 are numbers satisfying  $0 \leq d_0 / (c_0 + d_0) \leq 0.2$ , a0, b0, c0 and d0 are numbers satisfying  $1.8 \leq (a_0 + b_0 + c_0 + d_0) \leq 2.2$ , and e0 and f0 are numbers satisfying  $0 \leq f_0 / (e_0 + f_0) \leq 0.035$  and  $3.6 \leq (e_0 + f_0) \leq 4.4$ .



[2]

wherein M<sup>11</sup> represents at least one element selected from the group consisting of a monovalent element, a divalent element except Eu, Mn and Mg, a trivalent element and a pentavalent element, in which the proportion of the divalent element is 80 mol% or more, the proportion of the sum of Ba, Ca and Sr is 40mol% or more, and the ratio (molar ratio) of Ca to the sum of Ba and Ca is from 0.2 to 0.9; M<sup>21</sup> represents a group of tetravalent elements containing Si and Ge in a total amount of 90 mol% or more; Z<sup>1</sup> is at least one element selected from

the group consisting of a minus monovalent and minus divalent elements, H and N; and a1 is a number satisfying  $0.001 \leq a1 \leq 0.8$ , b1 is a number satisfying  $0 < b1 \leq 0.8$ , c1 and d1 are numbers satisfying  $0 < c1 / (c1 + d1) \leq 0.2$ , a1, b1, c1 and d1 are numbers satisfying  $1.8 \leq (a1 + b1 + c1 + d1) \leq 2.2$ , and e1 and f1 are numbers satisfying  $0 \leq f1 / (e1 + f1) \leq 0.035$  and  $3.6 \leq (e1 + f1) \leq 4.4$ .



[3]

wherein  $\text{M}^{12}$  represents at least one element selected from the group consisting of a monovalent element, a divalent element except Eu, Mn and Mg, a trivalent element and a pentavalent element, in which the proportion of the divalent element is 80 mol% or more, the proportion of the sum of Ba, Ca and Sr is 40 mol% or more, and the ratio (molar ratio) of Ca to the sum of Ba and Ca is less than 0.2;  $\text{M}^{22}$  represents a group of tetravalent elements containing Si and Ge in a total amount of 90 mol% or more;  $\text{Z}^2$  is at least one element selected from the group consisting of a minus monovalent and minus divalent elements, H and N; and a2 is a number satisfying  $0.01 \leq a2 \leq 0.8$ , b2 is a number satisfying  $0 < b2 \leq 0.8$ , c2 and d2 are numbers satisfying  $0 < c2 / (c2 + d2) \leq 0.2$  or  $0.3 \leq c2 / (c2 + d2) \leq 0.8$ , a2, b2, c2 and d2 are numbers satisfying  $1.8 \leq (a2 + b2 + c2 + d2) \leq 2.2$ , and e2 and f2 are numbers satisfying  $0 \leq f2 / (e2 + f2) \leq 0.035$  and  $3.6 \leq (e2 + f2) \leq 4.4$ .

According to the present invention, there is obtained a red or white phosphor having high luminance and from a bright tone to a deep tone, and there can be provided a light emitting device which efficiently emits visible light having high color rendering properties.

#### Brief Description of the Drawings

Fig. 1 is a view showing one example of a light emitting device in which a film-like phosphor is allowed to contact with or formed on a surface emitting type GaN-based diode.

Fig. 2 is a schematic cross sectional view showing one example of a light emitting device comprising a phosphor in the present invention and a first light emitter (350 nm to 430 nm light emitter).

Fig. 3 is a schematic cross sectional view showing one example of a surface emitting lighting system of the present invention.

Fig. 4 is an emission spectrum of a phosphor of Example A-3 at the time when it has irradiated with light of 400 nm which is a main wavelength in an ultraviolet light region of a GaN-based light emitting diode.

Fig. 5 is an emission spectrum of a phosphor of Example A-4 at the time when it has irradiated with light of 400 nm which is a main wavelength in an ultraviolet light region of

a GaN-based light emitting diode.

Fig. 6 is a graph showing a method for measuring the half-value width of a peak group.

Fig. 7 shows the results of X-ray diffraction measurement of a phosphor of Example A-8.

Fig. 8 is a graph showing emission spectra at the time when phosphors of Example A-8, Example A-9, Example A-10 and Example A-11 have each been irradiated with light of 400 nm which is a main wavelength in a near-ultraviolet region of a GaN-based light emitting diode.

Fig. 9 is an emission spectrum of a phosphor of Example B-2 at the time when it has irradiated with light of 400 nm which is a main wavelength in an ultraviolet light region of a GaN-based light emitting diode.

Fig. 10 shows the results of X-ray diffraction measurement of a phosphor of Example B-3.

Fig. 11 is a graph showing emission spectra at the time when phosphors of Example B-3, Example B-4, Example B-5 and Example B-6 have each been irradiated with light of 400 nm which is a main wavelength in a near-ultraviolet light region of a GaN-based light emitting diode.

Fig. 12 is an emission spectrum of a phosphor of Example C-3 at the time when it has irradiated with light of 400 nm which is a main wavelength in an ultraviolet light region of a GaN-based light emitting diode.

Fig. 13 is an emission spectrum of a phosphor of Example C-4 at the time when it has irradiated with light of 400 nm which is a main wavelength in an ultraviolet light region of a GaN-based light emitting diode.

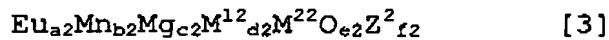
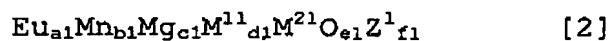
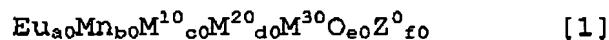
As for reference numerals in the figures, 1 indicates a second light emitter, 2 indicates a surface emitting type GaN-based LD, 3 indicates a substrate, 4 indicates a light emitting device, 5 indicates a mount lead, 6 indicates an inner lead, 7 indicates a first light emitter (350 nm to 430 nm light emitter), 8 indicates a resin portion allowed to contain a phosphor of the present invention, 9 indicates a conductive wire, 10 indicates a mold member, 11 indicates a surface emitting lighting system in which light emitting elements are incorporated, 12 indicates a holding case, 13 indicates a light emitting device, and 14 indicates a diffuser panel, respectively.

#### Best Mode for Carrying Out the Invention

Embodiments of the present invention will be illustrated in detail below, but the present invention is not limited to the following embodiments, and can be carried out with various variations within the scope of its gist.

The present invention is a phosphor comprising a crystal phase having a chemical composition of the following formula

[1], [2] or [3], and a light emitting device comprising the phosphor having a crystal phase having a chemical composition of the following formula [1], [2] or [3], and a light emitting source for irradiating it with light of 350 nm to 430 nm:



First, formula [1] will be illustrated.

$\text{M}^{10}$  in formula [1] is a divalent element containing 85 mol% or more of at least one element selected from the group consisting of Ba, Ca and Sr, in which the ratio (molar ratio) of Ca to the sum of Ba and Ca is from 0.1 to 0.9. That is to say, almost all or all of it consists of at least one element selected from the group consisting of Ba, Ca and Sr. Another divalent element can be contained within the range that the performance is not impaired, and examples thereof include V, Cr, Fe, Co, Ni, Cu, Zn, Mo, Ru, Pd, Ag, Cd, Sn, Sm, Tm, Yb, W, Re, Os, Ir, Pt, Hg, Pb and the like.  $\text{M}^{10}$  may contain at least one selected from the group of these elements at a ratio of 15 mol% or less in total. Of these, V, Zn, Mo, Sn, Sm, Tm, Yb, W, Pb and the like are difficult to have an influence on the performance, and can be contained in  $\text{M}^{10}$  at a ratio of 15 mol% or less in total.

In  $M^{10}$  in formula [1], the ratio (molar ratio) of Ca to the sum of Ba and Ca is from 0.1 to 0.9. However, in terms of emission intensity of a red color or a white color, and the like, the lower limit of the molar ratio of Ca to the sum of Ba and Ca is preferably 0.2 or more, and the upper limit is preferably 0.8 or less. The proportion of the sum of Ba and Ca in  $M^{10}$  is preferably 70 mol% or more, more preferably 90 mol% or more, and still more preferably 100 mol%.

$M^{20}$  in formula [1] represents at least one element selected from the group consisting of a monovalent, trivalent and pentavalent elements, and examples thereof include but are not limited to Li, Na, K, Rb, Cs, B, Al, Ga, In, P, Sb, Bi, Ta, Nb, Rh, trivalent rear earth elements such as Y and Sc, and the like. In the sense of assisting crystallization of the silicate by diffusion of the divalent element in  $M^{10}$  and activating elements  $Eu^{2+}$  and  $Mn^{2+}$  into a solid in burning, the monovalent, trivalent or pentavalent element can be introduced in small amounts as an element in  $M^{10}$ . The  $M^{20}$  constituent element comprises an element which mainly substitutes an  $M^{10}$  site, and  $d0/(c0+d0)$ , the ratio of the number of moles of  $M^{20}$  to the total number of moles of  $M^{10}$  and  $M^{20}$ , is  $0 \leq d0/(c0+d0) \leq 0.2$ . However, in terms of emission intensity of a red color or a white color, and the like, it is preferably  $0 \leq d0/(c0+d0) \leq 0.1$ , and more preferably  $d0/(c0+d0) = 0$ .

$M^{30}$  in formula [1] represents a group of tetravalent

elements containing Si and Ge in a total amount of 90 mol% or more. However, in terms of emission intensity of a red color or a white color, and the like, it is preferred that  $M^{30}$  contains Si in an amount of 80 mol% or more, and it is more preferred that  $M^{30}$  consists of Si. The tetravalent elements other than Si and Ge include Zn, Ti, Hf and the like. In terms of emission intensity of a red color or a white color, and the like, these may be contained within the range that the performance is not impaired.

$Z^0$  in formula [1] is at least one element selected from the group consisting of a minus monovalent and minus divalent elements, H and N. It may be, for example, F, Cl, Br, I or the like which is minus monovalent, as well as S, Se or Te which is the same minus divalent element as oxygen, and may contain an OH group. An oxygen group may be partially changed to an ON group or an N group. Further,  $Z^0$  may be contained to such a degree that it has a little influence on fluorescent performance, that is to say, at a ratio of about 2 mol% or less based on the total elements in the impurity level. This corresponds to 0.035 or less as the molar ratio of  $Z^0$  to ( $Z^0$  + oxygen atom). Accordingly, the range of  $f0/(e0+f0)$  which is the molar ratio of  $Z^0$  to ( $Z^0$  + oxygen atom) is  $0 \leq f0/(e0+f0) \leq 0.035$ . In terms of performance of the phosphor, it is preferably  $f0/(e0+f0) \leq 0.01$ , and preferably  $f0/(e0+f0) = 0$  in ordinary use.

As for the Eu molar ratio  $a_0$  in formula [1],  $a_0$  is a number satisfying  $0.001 \leq a_0 \leq 0.6$ . When the molar ratio  $a_0$  of a luminescent center ion  $\text{Eu}^{2+}$  is too small, the emission intensity tends to decrease. On the other hand, even when it is too large, the emission intensity also tends to decrease by a phenomenon called concentration quenching or temperature quenching. Accordingly, the lower limit is preferably  $0.005 \leq a_0$ , and more preferably  $0.02 \leq a_0$ , and the upper limit is more preferably  $a_0 \leq 0.5$ .

The Mn molar ratio  $b_0$  in formula [1] is a factor which has a decisive influence on selection of red light emission or white light emission. When  $b_0$  is 0, no red peak is obtained to give only a blue or blue-green peak. However, when  $b_0$  takes a small positive number, a red peak appears in blue and green peaks to give white light emission as a whole. When  $b_0$  takes a larger positive number, blue and green peaks almost disappear to mainly give a red peak. The range of  $b_0$  is  $0 < b_0 \leq 0.7$  as a red phosphor or a white phosphor. It is conceivable that the phosphor receives irradiation of an excitation light source to excite  $\text{Eu}^{+2}$ , and that the energy of  $\text{Eu}^{+2}$  excited thereby transfers to  $\text{Mn}^{+2}$ , which emits red light. The degree of energy transfer somewhat differs mainly according to the composition of  $\text{M}^{10}$  and  $\text{M}^{20}$ , so that the boundary value of  $b_0$  at which the red phosphor is changed to the white phosphor somewhat differs according to the composition of  $\text{M}^{10}$  and  $\text{M}^{20}$ . Accordingly, the

good ranges of  $b_0$  for red light emission and white light emission can not be strictly distinguished. However, it is preferably  $0 < b_0 \leq 0.2$ , and more preferably  $0.02 \leq b_0 \leq 0.2$ , as the white phosphor, and it is preferably  $0.05 \leq b_0 \leq 0.7$ , and more preferably  $0.1 \leq b_0 \leq 0.6$ , as the red phosphor.

In the crystal phase  $\text{Eu}_{a_0}\text{Mn}_{b_0}\text{M}^{10}_{-c_0}\text{M}^{20}_{-d_0}\text{M}^{30}_{-e_0}\text{O}_{e_0}\text{Z}^0_{f_0}$  in the above-mentioned formula [1],  $\text{Eu}^{2+}$  and  $\text{Mn}^{2+}$  are substituted by  $\text{M}^{10}$  comprising a divalent element,  $\text{M}^{30}$  is mainly occupied by Si, the anion is mainly oxygen,  $\text{M}^{20}$  comprises a monovalent, trivalent or pentavalent element other than divalent and tetravalent elements which are main elements, and the total molar ratios of  $(\text{M}^{10} + \text{M}^{20})$ ,  $\text{M}^{30}$  and oxygen atoms are 2, 1 and 4, respectively, in its basic composition. Even when cation deficiency or anion deficiency somewhat occurs, it has no significant influence on the desired fluorescent performance. Accordingly, when the total molar ratio of  $\text{M}^{30}$  mainly occupied by Si is fixed to 1 on the chemical formula, the molar ratio  $(a_0 + b_0 + c_0 + d_0)$  of  $(\text{M}^{10} + \text{M}^{20})$  is within the range of  $1.8 \leq (a_0 + b_0 + c_0 + d_0) \leq 2.2$ , and preferably  $(a_0 + b_0 + c_0 + d_0) = 2$  among others. Further,  $(e_0 + f_0)$  which is the total molar ratio of a site on the anion side is usually within the range of  $3.6 \leq (e_0 + f_0) \leq 4.4$ , and preferably  $e_0 = 4$  and  $f_0 = 0$  among others.

The phosphor used in the present invention can be produced by preparing a mixture of an  $\text{M}^{10}$  source, an  $\text{M}^{20}$  source and an  $\text{M}^{30}$  source as shown in the above-mentioned formula [1]

and element source compounds of Eu and Mn as activating elements by a mixing method of the following (A) or (B), and burning the mixture by heat treatment.

(A) A dry mixing method of combining pulverization using a dry pulverizer such as a hummer mill, a roll mill, a ball mill or a jet mill, or pulverization using a mortar and a pestle, and mixing using a mixer such as a ribbon blender, a V type blender or a Henschel mixer, or mixing using a mortar and a pestle.

(B) A wet mixing method of adding water or the like to form a slurry state or a solution state using a pulverizer or a mortar and a pestle, performing mixing by a pulverizer, a mortar and a pestle, an evaporating dish and a stirrer, or the like, and drying the mixture by spray drying, heat drying, air seasoning or the like.

Of these methods, particularly in the element source compounds for the activating elements, the use of a liquid medium is preferred because it is necessary to homogeneously mixing and dispersing small amounts of compounds over all. Further, also in that a mixture which is homogeneous over all is obtained for the other element source compounds, the latter wet method is preferred. Furthermore, the heat treatment method is conducted by performing heating in a heat-resistant container such as a crucible or tray using a material low in reactivity with the phosphor at a temperature of usually 750°C

to 1400°C, preferably 900°C to 1300°C, under a single or mixed atmosphere of gases such as carbon monoxide, carbon dioxide, nitrogen, hydrogen and argon for 10 minutes to 24 hours. Washing, drying, classification treatment and the like are performed after the heat treatment as needed.

As the above-mentioned heating atmosphere, there is selected an atmosphere which is necessary for obtaining an ion state (valence) in which the activating element contributes to light emission. In the case of divalent Eu and Mn and the like in the present invention, heating under a neutral or reducing atmosphere of carbon monoxide, nitrogen, hydrogen, argon or the like is preferred, and heating under a reducing atmosphere containing carbon monoxide or hydrogen is more preferred. The existence of carbon in the atmosphere is still more preferred. Specifically, it is achieved by heating with a carbon heater furnace, heating using a container such as a crucible made of carbon, under a reducing atmosphere, heating with the coexistence of carbon beads or the like in a reducing atmosphere, and the like.

The  $M^{10}$  sources, the  $M^{20}$  sources, the  $M^{30}$  sources and the element source compounds of the activating elements include an oxide, a hydroxide, a carbonate, a nitrate, a sulfate, an oxalate, a carboxylate, a halide and the like of  $M^{10}$ ,  $M^{20}$ ,  $M^{30}$  and the activating element, respectively, and are selected from these, considering reactivity with a complex oxide,

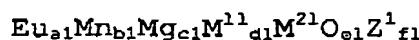
non-occurrence of  $\text{NO}_x$ ,  $\text{SO}_x$  and the like, and the like.

Specifically exemplifying the  $M^{10}$  source compounds for the above-mentioned Ba, Ca and Sr cited as  $M^{10}$ , the Ba source compounds include  $\text{BaO}$ ,  $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ ,  $\text{BaCO}_3$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{BaSO}_4$ ,  $\text{Ba}(\text{OCO})_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Ba}(\text{OCOCH}_3)_2$ ,  $\text{BaCl}_2$  and the like, the Ca source compounds include  $\text{CaO}$ ,  $\text{Ca(OH)}_2$ ,  $\text{CaCO}_3$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{Ca}(\text{OCO})_2 \cdot \text{H}_2\text{O}$ ,  $\text{Ca}(\text{OCOCH}_3)_2 \cdot \text{H}_2\text{O}$ ,  $\text{CaCl}_2$  and the like, and the Sr source compounds include  $\text{SrO}$ ,  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ ,  $\text{SrCO}_3$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{SrSO}_4$ ,  $\text{Sr}(\text{OCO})_2 \cdot \text{H}_2\text{O}$ ,  $\text{Sr}(\text{OCOCH}_3)_2 \cdot 0.5\text{H}_2\text{O}$ ,  $\text{SrCl}_2$  and the like.

Specifically exemplifying the  $M^{30}$  source compounds for the above-mentioned Si and Ge cited as  $M^{30}$ , the Si source compounds include  $\text{SiO}_2$ ,  $\text{H}_4\text{SiO}_4$ ,  $\text{Si}(\text{OCOCH}_3)_4$  and the like, and the Ge source compounds include  $\text{GeO}_2$ ,  $\text{Ge}(\text{OH})_4$ ,  $\text{Ge}(\text{OCOCH}_3)_4$ ,  $\text{GeCl}_4$  and the like.

Further, specifically exemplifying the element source compounds for the above-mentioned Eu and Mn cited as the activating elements, they include  $\text{Eu}_2\text{O}_3$ ,  $\text{Eu}_2(\text{SO}_4)_3$ ,  $\text{Eu}_2(\text{OCO})_6$ ,  $\text{EuCl}_2$ ,  $\text{EuCl}_3$ ,  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{MnO}_2$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{MnO}$ ,  $\text{Mn}(\text{OH})_2$ ,  $\text{MnCO}_3$ ,  $\text{Mn}(\text{OCOCH}_3)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Mn}(\text{OCOCH}_3)_3 \cdot \text{nH}_2\text{O}$ ,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  and the like.

Then, the following formula [2] will be illustrated.



[2]

$M^{11}$  in formula [2] represents at least one element selected from the group consisting of a monovalent element, a divalent element except Eu, Mn and Mg, a trivalent element and a pentavalent element, and satisfies conditions that the proportion of the divalent element is 80 mol% or more, that the proportion of the sum of Ba, Ca and Sr is 40 mol% or more, and that the ratio (molar ratio) of Ca to the sum of Ba and Ca is from 0.2 to 0.9. Specifically describing the elements other than Ba, Ca and Sr, the monovalent elements include Li, Na, K, Rb, Cs and the like, the divalent elements include V, Cr, Fe, Co, Ni, Cu, Zn, Mo, Ru, Pd, Ag, Cd, Sn, Sm, Tm, Yb, W, Re, Os, Ir, Pt, Hg, Pb and the like, the trivalent elements include B, Al, Ga, In and the like, and a rare earth element such as Y or Sc, and the pentavalent elements include P, Sb and Bi. However, they are not limited thereto. Above all, in the divalent elements, V, Zn, Mo, Sn, Sm, Tm, Yb, W and Pb are difficult to have an influence on the performance.

In the sense of assisting crystallization of the silicate by diffusion of the divalent element in  $M^{11}$  and activating elements  $Eu^{2+}$  and  $Mn^{2+}$  into a solid in burning, the monovalent, trivalent or pentavalent element may be introduced in a total amount of 20 mol% or less. In terms of emission intensity of a red color or a white color, and the like, the ratio (molar ratio) of Ca to the sum of Ba and Ca is preferably from 0.2 to 0.8. In terms of emission intensity of a red color

or a white color, and the like, the proportion of the sum of Ba, Ca and Sr is preferably 80 mol% or more, more preferably the proportion of the sum of Ba and Ca is 80 mol% or more, and still more preferably the proportion of the sum of Ba, Ca and Sr is 100 mol%.

$M^{21}$  in formula [2] represents a group of tetravalent elements containing Si and Ge in a total amount of 90 mol% or more. However, in terms of emission intensity of a red color or a white color, and the like, it is preferred that  $M^{21}$  contains Si in an amount of 80 mol% or more, and it is more preferred that  $M^{21}$  consists of Si. The tetravalent elements other than Si and Ge include Zn, Ti, Hf and the like. In terms of emission intensity of a red color or a white color, and the like, these may be contained within the range that the performance is not impaired.

$Z^1$  in formula [2] is at least one element selected from the group consisting of a minus monovalent and minus divalent elements, H and N. It may be, for example, F, Cl, Br, I or the like which is minus monovalent, as well as S, Se or Te which is the same minus divalent element as oxygen, and may contain an OH group. An oxygen group may be partially changed to an ON group or an N group. Further,  $Z^1$  may be contained to such a degree that it has a little influence on fluorescent performance, that is to say, at a ratio of about 2 mol% or less based on the total elements in the impurity level. This

corresponds to 0.035 or less as the molar ratio of  $Z^1$  to ( $Z^1$  + oxygen atom). Accordingly, the range of  $f1/(e1+f1)$  which is the molar ratio of  $Z^1$  to ( $Z^1$  + oxygen atom) is  $0 \leq f1/(e1+f1) \leq 0.035$ . In terms of performance of the phosphor, it is preferably  $f1/(e1+f1) \leq 0.01$ , and preferably  $f1/(e1+f1) = 0$ .

As for the Eu molar ratio  $a1$  in formula [2],  $a1$  is a number satisfying  $0.001 \leq a1 \leq 0.8$ . When the molar ratio  $a1$  of a luminescent center ion  $\text{Eu}^{2+}$  is too small, the emission intensity tends to decrease. On the other hand, even when it is too large, the emission intensity also tends to decrease by a phenomenon called concentration quenching or temperature quenching. Accordingly, the lower limit is preferably  $0.005 \leq a1$ , and more preferably  $0.02 \leq a1$ , and the upper limit is more preferably  $a1 \leq 0.5$ .

The Mn molar ratio  $b1$  in formula [2] is a factor which has a decisive influence on selection of red light emission or white light emission. When  $b1$  is 0, no red peak is obtained to give only a blue or blue-green peak. However, when  $b1$  takes a small positive number, a red peak appears in blue and green peaks to give white light emission as a whole. When  $b1$  takes a larger positive number, blue and green peaks almost disappear to mainly give a red peak. The range of  $b1$  is  $0 < b1 \leq 0.8$  as a red phosphor or a white phosphor. It is conceivable that the phosphor receives irradiation of an excitation light source to excite  $\text{Eu}^{+2}$ , and that the energy of  $\text{Eu}^{+2}$  excited thereby

transfers to  $Mn^{+2}$ , which emits red light. The degree of energy transfer somewhat differs mainly according to the composition of  $M^{11}$  and  $M^{21}$ , so that the boundary value of  $b_1$  at which the red phosphor is changed to the white phosphor somewhat differs according to the composition of  $M^{11}$  and  $M^{21}$ . Accordingly, the good ranges of  $b_1$  for red light emission and white light emission can not be strictly distinguished. However, it is preferably  $0 < b_1 \leq 0.15$ , and more preferably  $0.01 \leq b_1 \leq 0.15$ , as the white phosphor, and it is preferably  $0.03 \leq b_1 \leq 0.8$ , and more preferably  $0.06 \leq b_1 \leq 0.4$ , as the red phosphor.

Mg in formula [2] is substituted by  $M^{11}$  mainly comprising a divalent element, and  $c_1/(c_1+d_1)$ , the ratio of the number of moles of Mg to the total number of moles of Mg and  $M^{11}$ , is  $0 < c_1/(c_1+d_1) \leq 0.2$ . However, in terms of emission intensity of a red color or a white color, and the like, it is preferably  $0 < c_1/(c_1+d_1) \leq 0.7$ .

In the crystal phase  $Eu_{a_1}Mn_{b_1}Mg_{c_1}M^{11}_{d_1}M^{21}_{e_1}O_{e_1}Z^1_{f_1}$  in the above-mentioned formula [2],  $Eu^{2+}$ ,  $Mn^{2+}$  and  $Mg^{+2}$  are substituted by  $M^{11}$  mainly comprising a divalent element,  $M^{21}$  is mainly occupied by Si and Ge, the anion is mainly oxygen, and the total molar ratios of  $M^{11}$ ,  $M^{21}$  and oxygen atoms are 2, 1 and 4, respectively, in its basic composition. Even when cation deficiency or anion deficiency somewhat occurs, it has no significant influence on the desired fluorescent performance.

Accordingly, when the total molar ratio of  $M^{21}$  mainly occupied by Si and Ge is fixed to 1 on the chemical formula, the molar ratio  $(a_1+b_1+c_1+d_1)$  of  $(M^{11}+Eu+Mn+Mg)$  is within the range of  $1.8 \leq (a_1+b_1+c_1+d_1) \leq 2.2$ , preferably from 1.9 to 2.1, and more preferably  $(a_1+b_1+c_1+d_1)=2$ . Further,  $(e_1+f_1)$  which is the total molar ratio of a site on the anion side is within the range of  $3.6 \leq (e_1+f_1) \leq 4.4$ , preferably from 3.8 to 4.2, and more preferably  $e_1=4$  and  $f_1=0$ .

The phosphor used in the present invention can be produced by preparing a mixture of an  $M^{11}$  source, an  $M^{21}$  source and a Mg source as shown in the above-mentioned formula [2] and element source compounds of Eu and Mn as activating elements by a mixing method of the following (A) or (B), and burning the mixture by heat treatment.

(A) A dry mixing method of combining pulverization using a dry pulverizer such as a hummer mill, a roll mill, a ball mill or a jet mill, or pulverization using a mortar and a pestle, and mixing using a mixer such as a ribbon blender, a V type blender or a Henschel mixer, or mixing using a mortar and a pestle.

(B) A wet mixing method of adding water or the like to form a slurry state or a solution state using a pulverizer or a mortar and a pestle, performing mixing by a pulverizer, a mortar and a pestle, an evaporating dish and a stirrer, or the like, and drying the mixture by spray drying, heat drying, air

seasoning or the like.

Of these mixing methods, particularly in the element source compounds for the activating elements, the use of a liquid medium is preferred because it is necessary to homogeneously mixing and dispersing small amounts of compounds over all. Further, also in that a mixture which is homogeneous over all is obtained for the other element source compounds, the latter wet method is preferred. Furthermore, the heat treatment method is conducted by performing heating in a heat-resistant container such as a crucible or tray using a material low in reactivity with the phosphor at a temperature of usually 750°C to 1400°C, preferably 900°C to 1300°C, under a single or mixed atmosphere of gases such as carbon monoxide, carbon dioxide, nitrogen, hydrogen and argon for 10 minutes to 24 hours. Washing, drying, classification treatment and the like are performed after the heat treatment as needed.

As the above-mentioned heating atmosphere, there is selected an atmosphere which is necessary for obtaining an ion state (valence) in which the activating element contributes to light emission. In the case of divalent Eu and Mn and the like in the present invention, heating under a neutral or reducing atmosphere of carbon monoxide, nitrogen, hydrogen, argon or the like is preferred, and heating under a reducing atmosphere containing carbon monoxide or hydrogen is more

preferred. The existence of carbon in the atmosphere is still more preferred. Specifically, it is achieved by heating with a carbon heater furnace, heating using a container such as a crucible made of carbon, under a reducing atmosphere, heating with the coexistence of carbon beads or the like in a reducing atmosphere, and the like.

The  $M^{11}$  sources, the  $M^{21}$  sources, the Mg sources and the element source compounds of the activating elements include an oxide, a hydroxide, a carbonate, a nitrate, a sulfate, an oxalate, a carboxylate, a halide and the like of  $M^{11}$ ,  $M^{21}$ , Mg and the activating element, respectively, and are selected from these, considering reactivity with a complex oxide, non-occurrence of  $NO_x$ ,  $SO_x$  and the like, and the like.

Specifically exemplifying the  $M^{11}$  source compounds for the above-mentioned Ba, Ca and Sr cited as  $M^{11}$ , the Ba source compounds include  $BaO$ ,  $Ba(OH)_2 \cdot 8H_2O$ ,  $BaCO_3$ ,  $Ba(NO_3)_2$ ,  $BaSO_4$ ,  $Ba(OCO)_2 \cdot 2H_2O$ ,  $Ba(OCOCH_3)_2$ ,  $BaCl_2$  and the like, the Ca source compounds include  $CaO$ ,  $Ca(OH)_2$ ,  $CaCO_3$ ,  $Ca(NO_3)_2 \cdot 4H_2O$ ,  $CaSO_4 \cdot 2H_2O$ ,  $Ca(OCO)_2 \cdot H_2O$ ,  $Ca(OCOCH_3)_2 \cdot H_2O$ ,  $CaCl_2$  and the like, and the Sr source compounds include  $SrO$ ,  $Sr(OH)_2 \cdot 8H_2O$ ,  $SrCO_3$ ,  $Sr(NO_3)_2$ ,  $SrSO_4$ ,  $Sr(OCO)_2 \cdot H_2O$ ,  $Sr(OCOCH_3)_2 \cdot 0.5H_2O$ ,  $SrCl_2$  and the like.

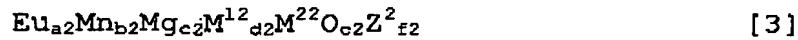
Specifically exemplifying the  $M^{21}$  source compounds for the above-mentioned Si and Ge cited as  $M^{21}$ , the Si source compounds include  $SiO_2$ ,  $H_4SiO_4$ ,  $Si(OCOCH_3)_4$  and the like, and

the Ge source compounds include  $\text{GeO}_2$ ,  $\text{Ge(OH)}_4$ ,  $\text{Ge(OCOCH}_3)_4$ ,  $\text{GeCl}_4$  and the like.

Specifically exemplifying the Mg source compounds for Mg, they include  $\text{MgO}$ ,  $\text{Mg(OH)}_2$ ,  $\text{MgCO}_3$ ,  $\text{Mg(OH)}_2\cdot 3\text{MgCO}_3\cdot 3\text{H}_2\text{O}$ ,  $\text{Mg(NO}_3)_2\cdot 6\text{H}_2\text{O}$ ,  $\text{MgSO}_4$ ,  $\text{Mg(OCO)}_2\cdot 2\text{H}_2\text{O}$ ,  $\text{Mg(OCOCH}_3)_2\cdot 4\text{H}_2\text{O}$ ,  $\text{MgCl}_2$  and the like.

Further, specifically exemplifying the element source compounds for the above-mentioned Eu and Mn cited as the activating elements, they include  $\text{Eu}_2\text{O}_3$ ,  $\text{Eu}_2(\text{SO}_4)_3$ ,  $\text{Eu}_2(\text{OCO})_6$ ,  $\text{EuCl}_2$ ,  $\text{EuCl}_3$ ,  $\text{Eu(NO}_3)_3\cdot 6\text{H}_2\text{O}$ ,  $\text{Mn(NO}_3)_2\cdot 6\text{H}_2\text{O}$ ,  $\text{MnO}_2$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{MnO}$ ,  $\text{Mn(OH)}_2$ ,  $\text{MnCO}_3$ ,  $\text{Mn(OCOCH}_3)_2\cdot 2\text{H}_2\text{O}$ ,  $\text{Mn(OCOCH}_3)_3\cdot \text{nH}_2\text{O}$ ,  $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$  and the like.

Then, the following formula [3] will be illustrated.



$\text{M}^{12}$  in formula [3] represents at least one element selected from the group consisting of a monovalent element, a divalent element except Eu, Mn and Mg, a trivalent element and a pentavalent element, and satisfies conditions that the proportion of the divalent element is 80 mol% or more, that the proportion of the sum of Ba, Ca and Sr is 40 mol% or more, and that the ratio (molar ratio) of Ca to the sum of Ba and Ca is less than 0.2.

Specifically describing the elements other than Ba, Ca and Sr, the monovalent elements include Li, Na, K, Rb, Cs and the like, the divalent elements include V, Cr, Fe, Co, Ni, Cu, Zn, Mo, Ru, Pd, Ag, Cd, Sn, Sm, Tm, Yb, W, Re, Os, Ir, Pt, Hg, Pb and the like, the trivalent elements include B, Al, Ga, In and the like, and a rare earth element such as Y or Sc, and the pentavalent elements include P, Sb, Bi and the like. However, they are not limited thereto. Above all, in the divalent elements, V, Zn, Mo, Sn, Sm, Tm, Yb, W and Pb are difficult to have an influence on the performance.

In the sense of assisting crystallization of the silicate by diffusion of the divalent element in  $M^{12}$  and activating elements  $Eu^{2+}$  and  $Mn^{2+}$  into a solid in burning, the monovalent, trivalent or pentavalent element may be introduced in a total amount of 20 mol% or less.

In terms of a deep red component and the like, the ratio (molar ratio) of Ca to the sum of Ba and Ca is preferably less than 0.1, and more preferably 0. In terms of emission intensity of a red color or a white color, and the like, the proportion of the sum of Ba, Ca and Sr is preferably 80 mol% or more, more preferably the proportion of the sum of Ba and Ca is 80 mol% or more, and still more preferably the proportion of the sum of Ba, Ca and Sr is 100 mol%.

$M^{22}$  in formula [3] represents a group of tetravalent elements containing Si and Ge in a total amount of 90 mol% or

more. However, in terms of emission intensity of a red color or a white color, and the like, it is preferred that  $M^{22}$  contains Si in an amount of 80 mol% or more, and it is more preferred that  $M^{22}$  consists of Si. The tetravalent elements other than Si and Ge include Zn, Ti, Hf and the like. In terms of emission intensity of a red color or a white color, and the like, these may be contained within the range that the performance is not impaired.

$Z^2$  in formula [3] is at least one element selected from the group consisting of a minus monovalent and minus divalent elements, H and N. It may be, for example, F, Cl, Br, I or the like which is minus monovalent, as well as S, Se or Te which is the same minus divalent element as oxygen, and may contain an OH group. An oxygen group may be partially changed to an ON group or an N group. Further,  $Z^2$  may be contained to such a degree that it has a little influence on fluorescent performance, that is to say, at a ratio of about 2 mol% or less based on the total elements in the impurity level. This corresponds to 0.035 or less as the molar ratio of  $Z^2$  to ( $Z^2$  + oxygen atom). Accordingly, the range of  $f_2/(e_2+f_2)$  which is the molar ratio of  $Z^2$  to ( $Z^2$  + oxygen atom) is  $0 \leq f_2/(e_2+f_2) \leq 0.035$ . In terms of performance of the phosphor, it is preferably  $f_2/(e_2+f_2) \leq 0.01$ , and preferably  $f_2/(e_2+f_2) = 0$ .

As for the Eu molar ratio  $a_2$  in formula [3],  $a_2$  is a

number satisfying  $0.01 < a_2 \leq 0.8$ . When the molar ratio  $a_2$  of a luminescent center ion  $\text{Eu}^{2+}$  is too small, the emission intensity tends to decrease, preferably 0.001 or more, more preferably 0.01 or more. On the other hand, even when it is too large, the emission intensity also tends to decrease by a phenomenon called concentration quenching or temperature quenching. The upper limit is more preferably  $a_2 \leq 0.5$ .

The Mn molar ratio  $b_2$  in formula [3] is a factor which has a decisive influence on selection of red light emission or white light emission. When  $b_2$  is 0, no red peak is obtained to give only a blue or blue-green peak. However, when  $b_2$  takes a small positive number, a red peak appears in blue and green peaks to give white light emission as a whole. When  $b_2$  takes a larger positive number, blue and green peaks almost disappear to mainly give a red peak. The range of  $b_2$  is  $0 < b_2 \leq 0.8$  as a red phosphor or a white phosphor. It is conceivable that the phosphor receives irradiation of an excitation light source to excite  $\text{Eu}^{+2}$ , and that the energy of  $\text{Eu}^{+2}$  excited thereby transfers to  $\text{Mn}^{+2}$ , which emits red light. The degree of energy transfer somewhat differs mainly according to the composition of  $M^{12}$  and  $M^{22}$ , so that the boundary value of  $b_2$  at which the red phosphor is changed to the white phosphor somewhat differs according to the composition of  $M^{12}$  and  $M^{22}$ . Accordingly, the good ranges of  $b_2$  for red light emission and white light emission can not be strictly distinguished. However, in terms

of intensity of a luminescent color including the red color and the white color, and the like, it is more preferably  $0.002 \leq b_2 \leq 0.6$ , and still more preferably  $0.005 \leq b_2 \leq 0.4$ . In the present invention, the term "white color" should be broadly interpreted, and means that two or more maximum values exist in an emission spectrum, and each is a broad band emission peak.

Mg in formula [3] is substituted by  $M^{12}$  mainly comprising a divalent element, and  $c_2/(c_2+d_2)$ , the ratio of the number of moles of Mg to the total number of moles of Mg and  $M^{12}$ , is  $0 < c_2/(c_2+d_2) \leq 0.2$  or  $0.3 \leq c_2/(c_2+d_2) \leq 0.8$ . However, in terms of emission intensity of a red color or a white color, and the like, it is preferably  $0 < c_2/(c_2+d_2) \leq 0.7$ .

In the crystal phase  $Eu_{a_2}Mn_{b_2}Mg_{c_2}M^{12}_{d_2}M^{22}_{e_2}O_{e_2}Z^2_{f_2}$  in the above-mentioned formula [3],  $Eu^{2+}$ ,  $Mn^{2+}$  and  $Mg^{+2}$  are substituted by  $M^{12}$  mainly comprising a divalent element,  $M^{22}$  is mainly occupied by Si and Ge, the anion is mainly oxygen, and the total molar ratios of  $M^{12}$ ,  $M^{22}$  and oxygen atoms are 2, 1 and 4, respectively, in its basic composition. Even when cation deficiency or anion deficiency somewhat occurs, it has no significant influence on the desired fluorescent performance. Accordingly, when the total molar ratio of  $M^{22}$  mainly occupied by Si and Ge is fixed to 1 on the chemical formula, the molar ratio  $(a_2+b_2+c_2+d_2)$  of  $(M^{12}+Eu+Mn+Mg)$  is within the range of  $1.8 \leq (a_2+b_2+c_2+d_2) \leq 2.2$ , preferably from 1.9 to 2.1, and more preferably  $(a_2+b_2+c_2+d_2)=2$ . Further,  $(e_2+f_2)$  which is the

total molar ratio of a site on the anion side is within the range of  $3.6 \leq (e2+f2) \leq 4.4$ , and more preferably  $e2=4$  and  $f2=0$ .

The phosphor used in the present invention can be produced by preparing a mixture of an  $M^{12}$  source, an  $M^{22}$  source and a Mg source as shown in the above-mentioned formula [3] and element source compounds of Eu and Mn as activating elements by a mixing method of the following (A) or (B), and burning the mixture by heat treatment.

(A) A dry mixing method of combining pulverization using a dry pulverizer such as a hummer mill, a roll mill, a ball mill or a jet mill, or pulverization using a mortar and a pestle, and mixing using a mixer such as a ribbon blender, a V type blender or a Henschel mixer, or mixing using a mortar and a pestle.

(B) A wet mixing method of adding water or the like to form a slurry state or a solution state using a pulverizer or a mortar and a pestle, performing mixing by a pulverizer, a mortar and a pestle, an evaporating dish and a stirrer, or the like, and drying the mixture by spray drying, heat drying, air seasoning or the like.

Of these methods, particularly in the element source compounds for the activating elements, the use of a liquid medium is preferred because it is necessary to homogeneously mixing and dispersing small amounts of compounds over all. Further, also in that a mixture which is homogeneous over all

is obtained for the other element source compounds, the latter wet method is preferred. Furthermore, the heat treatment method is conducted by performing heating in a heat-resistant container such as a crucible or tray using a material low in reactivity with the phosphor at a temperature of usually 750°C to 1400°C, preferably 900°C to 1300°C, under a single or mixed atmosphere of gases such as carbon monoxide, carbon dioxide, nitrogen, hydrogen and argon for 10 minutes to 24 hours. Washing, drying, classification treatment and the like are performed after the heat treatment as needed.

As the above-mentioned heating atmosphere, there is selected an atmosphere which is necessary for obtaining an ion state (valence) in which the activating element contributes to light emission. In the case of divalent Eu and Mn and the like in the present invention, heating under a neutral or reducing atmosphere of carbon monoxide, nitrogen, hydrogen, argon or the like is preferred, and heating under a reducing atmosphere containing carbon monoxide or hydrogen is more preferred. The existence of carbon in the atmosphere is still more preferred. Specifically, it is achieved by heating with a carbon heater furnace, heating using a container such as a crucible made of carbon, under a reducing atmosphere, heating with the coexistence of carbon beads or the like in a reducing atmosphere, and the like.

The M<sup>12</sup> sources, the M<sup>22</sup> sources, the Mg sources and the

element source compounds of the activating elements include an oxide, a hydroxide, a carbonate, a nitrate, a sulfate, an oxalate, a carboxylate, a halide and the like of  $M^{12}$ ,  $M^{22}$ , Mg and the activating element, respectively, and are selected from these, considering reactivity with a complex oxide, non-occurrence of  $NO_x$ ,  $SO_x$  and the like, and the like.

Specifically exemplifying the  $M^{12}$  source compounds for the above-mentioned Ba, Ca and Sr cited as  $M^{12}$ , the Ba source compounds include  $BaO$ ,  $Ba(OH)_2 \cdot 8H_2O$ ,  $BaCO_3$ ,  $Ba(NO_3)_2$ ,  $BaSO_4$ ,  $Ba(OCO)_2 \cdot 2H_2O$ ,  $Ba(OCOCH_3)_2$ ,  $BaCl_2$  and the like, the Ca source compounds include  $CaO$ ,  $Ca(OH)_2$ ,  $CaCO_3$ ,  $Ca(NO_3)_2 \cdot 4H_2O$ ,  $CaSO_4 \cdot 2H_2O$ ,  $Ca(OCO)_2 \cdot H_2O$ ,  $Ca(OCOCH_3)_2 \cdot H_2O$ ,  $CaCl_2$  and the like, and the Sr source compounds include  $SrO$ ,  $Sr(OH)_2 \cdot 8H_2O$ ,  $SrCO_3$ ,  $Sr(NO_3)_2$ ,  $SrSO_4$ ,  $Sr(OCO)_2 \cdot H_2O$ ,  $Sr(OCOCH_3)_2 \cdot 0.5H_2O$ ,  $SrCl_2$  and the like.

Specifically exemplifying the  $M^{22}$  source compounds for the above-mentioned Si and Ge cited as  $M^{22}$ , the Si source compounds include  $SiO_2$ ,  $H_4SiO_4$ ,  $Si(OCOCH_3)_4$  and the like, and the Ge source compounds include  $GeO_2$ ,  $Ge(OH)_4$ ,  $Ge(OCOCH_3)_4$ ,  $GeCl_4$  and the like.

Specifically exemplifying the Mg source compounds for Mg, they include  $MgO$ ,  $Mg(OH)_2$ ,  $MgCO_3$ ,  $Mg(OH)_2 \cdot 3MgCO_3 \cdot 3H_2O$ ,  $Mg(NO_3)_2 \cdot 6H_2O$ ,  $MgSO_4$ ,  $Mg(OCO)_2 \cdot 2H_2O$ ,  $Mg(OCOCH_3)_2 \cdot 4H_2O$ ,  $MgCl_2$  and the like.

Further, specifically exemplifying the element source compounds for the above-mentioned Eu and Mn cited as the

activating elements, they include  $\text{Eu}_2\text{O}_3$ ,  $\text{Eu}_2(\text{SO}_4)_3$ ,  $\text{Eu}_2(\text{OCO})_6$ ,  $\text{EuCl}_2$ ,  $\text{EuCl}_3$ ,  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{MnO}_2$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{MnO}$ ,  $\text{Mn}(\text{OH})_2$ ,  $\text{MnCO}_3$ ,  $\text{Mn}(\text{OCOCH}_3)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Mn}(\text{OCOCH}_3)_3 \cdot \text{nH}_2\text{O}$ ,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  and the like.

The inventors of this application have found that the phosphor having the specified crystal structure, in addition to the above-mentioned composition range, shows particularly high emission intensity, thus completing the present invention. The definition of the crystal structure is generally made using a crystal system, a space group or the like. However, in the crystal phase in the present invention, a change in the crystal system or the space group occurs by distortion of the crystal structure (delicate structural change) associated with a change in composition, so that a univocal structural definition can not be carried out. Then, an X-ray diffraction pattern necessary for specifying the crystal phase which contributes to light emission is disclosed. Usually, in order to specify the identity of crystal structures of two compounds by the X-ray diffraction pattern, the agreement in angles ( $2\theta$ ) of about 6 diffraction peaks including a highest diffraction peak based on its crystal structure is sufficient. However, when the constituent element ratios are different as the compounds of the present invention, the angles of the diffraction peaks shift even though the crystal structures are the same. Accordingly, the specific angles of the diffraction peaks can

not be defined as numerical values. Then, the present inventors have given attention to a plane spacing of the diffraction peak calculated using the Bragg equation, and have specified the angle range of the diffraction peak by the following indication method.

#### Bragg Equation

$$d = \lambda / \{2 \times \sin(\theta)\} \quad (\text{equation 1})$$

$$\theta = \arcsin\{\lambda / (2 \times d)\} \quad (\text{equation 2})$$

d: Plane spacing (angstrom)

$\theta$ : Bragg angle (°)

$\lambda$ : X-ray wavelength of CuK $\alpha$ =1.54184 angstroms

In addition, (Equation 2) is one into which (equation 1) is changed. When the plane spacing range of a reference diffraction peak is defined as 4.17 angstroms to 3.95 angstroms, the range of the diffraction angle ( $2\theta$ ) becomes 21.3° to 22.5° from (equation 2).

From the angle ( $\theta_0$ ) of the reference diffraction peak measured, the plane spacing ( $d_0$ ) of the reference diffraction peak becomes the following (equation 3) according to (equation 1).

$$d_0 = \lambda / \{2 \times \sin(\theta_0)\} \quad (\text{equation 3})$$

Five peaks other than the reference diffraction peak are taken as P1, P2, P3, P4 and P5 from the low angle side, and the angle ranges in which the respective peaks appear are in turn taken as R1, R2, R3, R4 and R5.

The angle range R1 in which P1 appears is determined as follows. When a diffraction plane has a plane spacing of 0.720 time the plane spacing (d0) derived from the reference diffraction peak, and the deviation of the plane spacing associated with strain of the structure is taken as 1.5%, the start angle (R1s) and end angle (R1e) of the angle range R1 are derived from (equation 1) as follows:

$$R1s: 2 \times \arcsin\{\lambda / (2 \times d0 \times 0.720 \times 1.015)\}$$

$$R1e: 2 \times \arcsin\{\lambda / (2 \times d0 \times 0.720 \times 0.985)\}$$

Substitution of (equation 3) in each results in the following:

$$R1s: 2 \times \arcsin\{\sin(\theta_0) / (0.720 \times 1.015)\}$$

$$R1e: 2 \times \arcsin\{\sin(\theta_0) / (0.720 \times 0.985)\}$$

When hereinafter in the same way, the angle ranges in which P2, P3, P4 and P5 appear are defined as 0.698 time, 0.592 time, 0.572 time and 0.500 time, respectively, the plane spacing derived from the reference diffraction peak, and the deviation of the plane spacing associated with strain of the

structure is taken as 1.5% without variation, the respective angle ranges become as follows:

```
R2s: 2×arcsin{sin(θ0)/(0.698×1.015)}  
R2e: 2×arcsin{sin(θ0)/(0.698×0.985)}  
R3s: 2×arcsin{sin(θ0)/(0.592×1.015)}  
R3e: 2×arcsin{sin(θ0)/(0.592×0.985)}  
R4s: 2×arcsin{sin(θ0)/(0.572×1.015)}  
R4e: 2×arcsin{sin(θ0)/(0.572×0.985)}  
R5s: 2×arcsin{sin(θ0)/(0.500×1.015)}  
R5e: 2×arcsin{sin(θ0)/(0.500×0.985)}
```

That is to say, for the results of X-ray diffraction measurement thus obtained, the presence of the specified crystal structure as defined in the present invention can be confirmed by confirming that the respective peaks from the reference peak P0 to P5 appear in the above-mentioned angle ranges. This crystal phase is a crystal phase different from merwinite described in non-patent document 1 and non-patent document 2. The above-mentioned angle ranges R1 to R5 are more preferably as follows in which the deviation of the plane spacing associated with strain of the structure is taken as 1.0% without variation.

```
R1: 2×arcsin{sin(θ0)/(0.720×1.010)} to  
2×arcsin{sin(θ0)/(0.720×0.990)}  
R2: 2×arcsin{sin(θ0)/(0.698×1.010)} to
```

```
2×arcsin{sin(θ0)/(0.698×0.990) }

    R3: 2×arcsin{sin(θ0)/(0.592×1.010) } to
2×arcsin{sin(θ0)/(0.592×0.990) }

    R4: 2×arcsin{sin(θ0)/(0.572×1.010) } to
2×arcsin{sin(θ0)/(0.572×0.990) }

    R5: 2×arcsin{sin(θ0)/(0.500×1.010) } to
2×arcsin{sin(θ0)/(0.500×0.990) }
```

Although a method for preparing the above-mentioned crystal phase which characterizes the present invention is not limited, the desired crystal phase can be obtained by using, for example, a raw material having a small particle size of 10  $\mu\text{m}$  or less, particularly a raw material in which silica contains no water, allowing local aggregates not to exist before burning, which are considered to be uneven in composition, and performing burning under a reducing atmosphere using a crucible made of carbon.

As described above, it has become clear that all the phosphors having high emission intensity which are obtained in the present invention contain the above-mentioned specified crystal phase. From this, it is true that they are a phosphor comprising a crystal phase of an alkali earth silicate containing at least one element selected from the group consisting of Ba, Sr, Ca and Mg, and a phosphor characterized

by containing the above-mentioned specified crystal phase.

In the present invention, a first light emitter which irradiates the above-mentioned phosphor with light emits light having a wavelength of 350 nm to 430 nm. Preferably, there is used a light emitter which emits light having the peak wavelength in the wavelength range of 350 nm to 430 nm. Specific examples of the first light emitters include a light emitting diode (LED), a laser diode (LD) and the like. In terms of low electric power consumption, a laser diode is more preferred. Above all, preferred is a GaN-based LED or LD using a GaN-based compound semiconductor. This is because the GaN-based LED or LD is markedly high in emission output and external quantum efficiency, compared to a SiC-based LED or the like which emits light in this region, and extremely bright light emission is obtained at extremely low electric power by combination with the above-mentioned phosphor. For example, the GaN-based LED or LD usually has an emission intensity of 100 times or more that of the SiC-based, for a current load of 20 mA. In the GaN-based LED or LD, one having an  $\text{Al}_x\text{Ga}_y\text{N}$  light emitting layer, a GaN light emitting layer or an  $\text{In}_x\text{Ga}_y\text{N}$  light emitting layer is preferred. In the GaN-based LED, of these, one having the  $\text{In}_x\text{Ga}_y\text{N}$  light emitting layer is particularly preferred because of its extremely high emission intensity. In the GaN-based LD, one having a multiple quantum well structure of the  $\text{In}_x\text{Ga}_y\text{N}$  layer and the GaN layer is

particularly preferred because of its extremely high emission intensity. In the above, the value of X+Y is usually a value ranging from 0.8 to 1.2. In the GaN-based LED, one in which the light emitting layer is doped with Zn or Si or dopant-free one is preferred in terms of controlling emission characteristics. The GaN-based LED has the light emitting layer, a p layer, an n layer, electrodes and a substrate as basic constituent elements. One having a hetero structure in which the light emitting layer is sandwiched between the n type and p type  $Al_xGa_yN$  layers, GaN layers,  $In_xGa_yN$  layers or the like is preferred because of its high emission efficiency, and further, one in which the hetero structure is formed into a quantum well structure is more preferred because of its higher emission efficiency.

In the present invention, it is particularly preferred to use a surface emitting type light emitter, particularly a surface emitting type GaN-based laser diode, as the first light emitter, because it results in enhancement of emission efficiency of the whole light emitting device. The surface emitting type light emitter is a light emitter having strong light emission in the surface direction of a film. In the surface emitting type GaN-based laser diode, light emission in the surface direction of the light emitting layer can be made stronger than that in the edge direction by controlling

the growth of crystals of the light emitting layer and the like and devising well a reflective layer and the like. The emission cross sectional area per unit emission amount can be increased by using the surface emitting type one, compared to the type of emitting light from the edges of the light emitting layer. As a result, when the phosphor of the second light emitter is irradiated with the light, the irradiation area can be extremely increased at the same amount of light to improve irradiation efficiency. Accordingly, stronger light emission can be obtained from the phosphor of the second light emitter.

When the surface emitting type one is used as the first light emitter, the second light emitter is preferably filmy. As a result, the light from the surface emitting type one has a sufficiently large cross sectional area, so that when the second light emitter is made filmy in its cross sectional direction, the cross sectional area of irradiation from the first light emitter to the phosphor increases per unit amount of the phosphor. Accordingly, the intensity of light emission from the phosphor can be more increased.

Further, when the surface emitting type one is used as the first light emitter and the filmy one is used as the second light emitter, it is preferred to take a form in which the second filmy light emitter is directly brought into contact with a light emitting surface of the first light emitter. The term "contact" as used herein means to make a state in which the

first light emitter and the second light emitter are in close contact with each other without the interposition of air or gas. As a result, the loss in the amount of light that the light from the first light emitter is reflected from a film surface of the second light emitter to ooze outside can be avoided, so that the emission efficiency of the whole device can be improved.

A schematic perspective view indicating positional relationship between a first light emitter and a second light emitter in one example of a light emitting device of the present invention is shown in Fig. 1. In Fig. 1, 1 designates a second filmy light emitter having the above-mentioned phosphor, 2 designates a surface emitting type GaN-based LD as the first light emitter, and 3 designates a substrate. In order to make a state in contact with each other, the LD 2 and the second light emitter 1 are each separately prepared, and surfaces thereof may be brought into contact with each other by an adhesive or another means, or the second light emitter may be formed as a film (molded) on a light emitting surface of the LD 2. As a result, the LD 2 and the second light emitter 1 can be put into a contact state.

The light from the first light emitter and the light from the second light emitter are usually directed in all directions. However, when a powder of the phosphor of the second light emitter is dispersed in a resin, the light is

partially reflected when the light goes out of the resin, thereby aligning the direction thereof to some degree. Accordingly, the light can be guided to the efficient direction to some degree, so that one in which the powder of the above-mentioned phosphor has been dispersed in the resin is preferably used. Further, when the phosphor is dispersed in the resin, the total irradiation area of the light from the first light emitter onto the second light emitter increases. It also has therefore the advantage of being able to increase emission intensity from the second light emitter. The resins which can be used in this case include various ones such as a silicon resin, an epoxy resin, a polyvinyl-based resin, a polyethylenic resin, a polypropylenic resin and a polyester-based resin. However, in terms of good dispersibility of the phosphor powder, preferred is a silicon resin or an epoxy resin.

When the powder of the second light emitter is dispersed in the resin, the weight ratio of the powder of the second light emitter to the whole of the powder and the resin is usually from 10% to 95%, preferably from 20% to 90%, and more preferably from 30% to 80%. When the phosphor is too much, emission efficiency decreases in some cases by aggregation of the powder. When it is too little, emission efficiency in turn decreases in some cases, because of absorption or scattering of the light by the resin.

The light emitting device of the present invention comprises the above-mentioned phosphor as a wavelength conversion material and the light emitting element which emits light of 350 nm to 430 nm. The above-mentioned phosphor absorbs the light of 350 nm to 430 nm emitted by the light emitting element to provide the light emitting device which has good color rendering properties without depending on use environment and can emit high-intensity visible light. The phosphor having the crystal phase of the present invention emits light in a wavelength region indicating a red color or a white color by irradiation with light from the first light emitter which emits the light of 350 nm to 430 nm. Then, the light emitting device of the present invention is suitable for a light emission source for a backlight source, a traffic signal or the like, an image display unit such as a color liquid crystal display, a lighting system such as surface light emission, or the like.

Illustrating the light emitting device of the present invention according to the drawing, Fig. 2 is a schematic cross sectional view showing one example of a light emitting device having a first light emitter (350 nm to 430nm light emitter) and a second light emitter, and 4 is the light emitting device, 5 is a mount lead, 6 is an inner lead, 7 is the first light emitter (light emitter of 350 nm to 430 nm), 8 is a phosphor-containing resin portion as the second light emitter,

9 is a conductive wire, and 10 is a mold member.

The light emitting device which is one example of the present invention has a general cannonball type form as shown in Fig. 2, and the first light emitter (350 nm to 430nm light emitter) 7 comprising a GaN-based light emitting diode and the like is fixed in an upper cup of the mount lead 5 by covering it with the phosphor-containing resin portion formed as the second light emitter by mixing and dispersing the phosphor in a binder such as a silicon resin, an epoxy resin or an acrylic resin, and pouring the dispersion into the cup. On the other hand, the first light emitter 7 and the mount lead 5, and the first light emitter 7 and the inner lead 6 are each conducted to each other with the conductive wire 9, and the whole thereof is covered and protected with the mold member 10 comprising an epoxy resin or the like.

Further, in a surface emitting lighting system 11 in which this light emitting element 1 is incorporated, many light emitting devices 13 are disposed on a bottom surface of a square holding case 12 whose inner surface is made light-impermeable such as a white smooth surface, a power source, a circuit and the like (not shown) for driving the light emitting devices 13 are disposed in the outside thereof, and a diffuser panel 14 such as a milk-white acrylic plate is fixed to a portion corresponding to a lid of the holding case 12 for homogenization of light emission, as shown in Fig. 3.

Then, the surface emitting lighting system 11 is driven to apply voltage to the first light emitter of the light emitting element 13, thereby allowing light of 350 nm to 430 nm to be emitted. The light emission is partially absorbed by the above-mentioned phosphor in the phosphor-containing resin portion as the second light emitter to emit visible light. On the other hand, light emission having high color rendering properties is obtained by color mixing with blue light and the like which have not been absorbed by the phosphor. This light passes through the diffuser panel 14, and exits upward in the drawing. Thus, illuminating light having uniform brightness in a surface of the diffuser panel 14 of the holding case 12 is obtained.

#### Examples

The present invention will be illustrated with reference to examples in more detail below, but the present invention should not be construed as being limited to the following examples within its gist.

#### Example A-1

An aqueous solution of  $\text{Ba}(\text{NO}_3)_2$ , an aqueous solution of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , an aqueous solution of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , an aqueous solution of  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and a suspension of colloidal silica ( $\text{SiO}_2$ ) (the molar ratio of  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,

$\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{SiO}_2$  is 0.64:0.96:0.2:0.2:1) were mixed in a platinum container and dried. Then, the mixture was burnt by heating under a stream of nitrogen gas containing 4% of hydrogen at 1050°C for 2 hours to produce a phosphor  $\text{Ba}_{0.64}\text{Ca}_{0.96}\text{Eu}_{0.2}\text{Mn}_{0.2}\text{SiO}_4$  (phosphor used in a second light emitter). An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The wavelength of an emission peak thereof, the intensity of the emission peak at the time when the intensity of an emission peak of Comparative Example A-2 described later is taken as 100 (hereinafter referred to as the relative intensity), and the half-value width are shown in Table 1. This phosphor has a sufficiently wide half-value width, gives good color rendering properties, and emits a light red color having a peak wavelength within the range of 590 nm to 620 nm. This reveals that this phosphor emits reddish light which feels bright.

#### Comparative Example A-1

A phosphor  $\text{Ba}_{0.72}\text{Ca}_{1.08}\text{Eu}_{0.2}\text{SiO}_4$  was produced in the same manner as in Example A-1 with the exception that an aqueous solution of  $\text{Ba}(\text{NO}_3)_2$ , an aqueous solution of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , an aqueous solution of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and a suspension of colloidal silica ( $\text{SiO}_2$ ) (the molar ratio of  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{SiO}_2$  is 0.72:1.08:0.2:1) were used as original

solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The wavelength, relative intensity and half-value width of an emission peak thereof are shown in Table 1. This shows that when Mn is not added in the composition of Example A-1, no red peak appears.

#### Comparative Example A-2

A phosphor  $Ba_{1.6}Eu_{0.2}Mn_{0.2}SiO_4$  was produced in the same manner as in Example A-1 with the exception that an aqueous solution of  $Ba(NO_3)_2$ , an aqueous solution of  $Eu(NO_3)_3 \cdot 6H_2O$ , an aqueous solution of  $Mn(NO_3)_2 \cdot 6H_2O$  and a suspension of colloidal silica ( $SiO_2$ ) (the molar ratio of  $Ba(NO_3)_2$ ,  $Eu(NO_3)_3 \cdot 6H_2O$ ,  $Mn(NO_3)_2 \cdot 6H_2O$  and  $SiO_2$  is 1.6:0.2:0.2:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The wavelength, relative intensity and half-value width of an emission peak thereof are shown in Table 1. This shows that when Ca is not added in the composition of Example A-1, no red peak appears.

#### Comparative Example A-3

A phosphor  $Ca_{1.6}Eu_{0.2}Mn_{0.2}SiO_4$  was produced in the same

manner as in Example A-1 with the exception that an aqueous solution of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , an aqueous solution of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , an aqueous solution of  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and a suspension of colloidal silica ( $\text{SiO}_2$ ) (the molar ratio of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{SiO}_2$  is 1.6:0.2:0.2:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The wavelength, relative intensity and half-value width of an emission peak thereof are shown in Table 1. This shows that when Ba is not added in the composition of Example A-1, no red peak appears.

#### Example A-2

A phosphor  $\text{Ba}_{0.84}\text{Ca}_{0.56}\text{Eu}_{0.3}\text{Mn}_{0.3}\text{SiO}_4$  was produced in the same manner as in Example A-1 with the exception that an aqueous solution of  $\text{Ba}(\text{NO}_3)_2$ , an aqueous solution of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , an aqueous solution of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , an aqueous solution of  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and a suspension of colloidal silica ( $\text{SiO}_2$ ) (the molar ratio of  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{SiO}_2$  is 0.84:0.56:0.3:0.3:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The wavelength, relative intensity and

half-value width of an emission peak thereof are shown in Table 1. This phosphor has a sufficiently wide half-value width, gives good color rendering properties, and emits a light red color having a peak wavelength within the range of 590 nm to 620 nm. This reveals that this phosphor emits reddish light which feels bright.

#### Example A-3

A phosphor  $Ba_{0.75}Ca_{0.5}Eu_{0.3}Mn_{0.45}SiO_4$  was produced in the same manner as in Example A-1 with the exception that an aqueous solution of  $Ba(NO_3)_2$ , an aqueous solution of  $Ca(NO_3)_2 \cdot 4H_2O$ , an aqueous solution of  $Eu(NO_3)_3 \cdot 6H_2O$ , an aqueous solution of  $Mn(NO_3)_2 \cdot 6H_2O$  and a suspension of colloidal silica ( $SiO_2$ ) (the molar ratio of  $Ba(NO_3)_2$ ,  $Ca(NO_3)_2 \cdot 4H_2O$ ,  $Eu(NO_3)_3 \cdot 6H_2O$ ,  $Mn(NO_3)_2 \cdot 6H_2O$  and  $SiO_2$  is 0.75:0.5:0.3:0.45:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The emission spectrum is shown in Fig. 4. In order to remove the influence of an excitation light source on the emission spectrum, the measurement was made introducing a filter for cutting light of 420 nm or less. The wavelength, relative intensity and half-value width of an emission peak thereof are shown in Table 1. This phosphor has a sufficiently wide half-value width, gives good color rendering properties,

and emits a light red color having a peak wavelength within the range of 590 nm to 620 nm. This reveals that this phosphor emits reddish light which feels bright.

Table 1

Example or Comparative Example	Chemical Composition of Phosphor	Wavelength of Emission Peak (nm)	Relative Intensity of Emission Peak	Half-Value Width of Emission Peak (nm)	Molar Ratio of Mn	Ratio of Ca to the Sum of Ba and Ca (molar ratio)
Example A-1	$\text{Ba}_{0.84}\text{Ca}_{0.16}\text{Eu}_{0.2}\text{Mn}_{0.2}\text{SiO}_4$	605	108	80	0.2	0.6
Example A-2	$\text{Ba}_{0.84}\text{Ca}_{0.16}\text{Eu}_{0.3}\text{Mn}_{0.3}\text{SiO}_4$	603	75	79	0.3	0.4
Example A-3	$\text{Ba}_{0.75}\text{Ca}_{0.5}\text{Eu}_{0.3}\text{Mn}_{0.45}\text{SiO}_4$	607	36	79	0.45	0.4
Comparative Example A-1	$\text{Ba}_{0.72}\text{Ca}_{1.08}\text{Eu}_{0.2}\text{SiO}_4$	448	99	104	0	0.6
Comparative Example A-2	$\text{Ba}_{1.0}\text{Eu}_{0.2}\text{Mn}_{0.2}\text{SiO}_4$	509	100	62	0.2	0
Comparative Example A-3	$\text{Ca}_{1.6}\text{Eu}_{0.2}\text{Mn}_{0.2}\text{SiO}_4$	512	25	85	0.2	1

**Example A-4**

A phosphor  $Ba_{1.11}Ca_{0.74}Eu_{0.06}Mn_{0.09}SiO_4$  was produced in the same manner as in Example A-1 with the exception that an aqueous solution of  $Ba(NO_3)_2$ , an aqueous solution of  $Ca(NO_3)_2 \cdot 4H_2O$ , an aqueous solution of  $Eu(NO_3)_3 \cdot 6H_2O$ , an aqueous solution of  $Mn(NO_3)_2 \cdot 6H_2O$  and a suspension of colloidal silica ( $SiO_2$ ) (the molar ratio of  $Ba(NO_3)_2$ ,  $Ca(NO_3)_2 \cdot 4H_2O$ ,  $Eu(NO_3)_3 \cdot 6H_2O$ ,  $Mn(NO_3)_2 \cdot 6H_2O$  and  $SiO_2$  is 1.11:0.74:0.06:0.09:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured.

An emission spectrum thereof is shown in Fig. 5. The x and y values of chromaticity coordinates indicating colors, the wavelength of the maximum peak, the intensity of the maximum peak of this phosphor at the time when the intensity of the maximum peak of a phosphor in Comparative Example A-5 described later is taken as 100 (hereinafter referred to as the relative intensity of the maximum peak), the ratio of the intensity at 600 nm to the intensity of the maximum peak, which gives an indication of to what extent a red component exists, and the half-value width of a group of peaks are shown in Table 2. This reveals that white light emission is obtained in which blue, green and red components all sufficiently exist, the spectrum width is very wide, and color rendering properties are high.

The maximum peak means a peak which is highest in intensity when a plurality of peaks exist in an emission spectrum, and in the case of a single peak, the maximum peak means itself. Further, the half-value width of a group of peaks gives an indication of how wide an emission spectrum distributes, and how high color rendering properties are, and is defined as the total of widths of wavelength regions having an intensity of half or more the intensity of the maximum peak in the spectrum, as shown in Fig. 6. For example, in Fig. 6, the half-value width of a group of peaks becomes the total of width B and width C.

#### Example A-5

A phosphor  $Ba_{0.68}Ca_{1.02}Eu_{0.2}Mn_{0.1}SiO_4$  was produced in the same manner as in Example A-1 with the exception that an aqueous solution of  $Ba(NO_3)_2$ , an aqueous solution of  $Ca(NO_3)_2 \cdot 4H_2O$ , an aqueous solution of  $Eu(NO_3)_3 \cdot 6H_2O$ , an aqueous solution of  $Mn(NO_3)_2 \cdot 6H_2O$  and a suspension of colloidal silica ( $SiO_2$ ) (the molar ratio of  $Ba(NO_3)_2$ ,  $Ca(NO_3)_2 \cdot 4H_2O$ ,  $Eu(NO_3)_3 \cdot 6H_2O$ ,  $Mn(NO_3)_2 \cdot 6H_2O$  and  $SiO_2$  is 0.68:1.02:0.2:0.1:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The x and y values of chromaticity coordinates, the wavelength of the maximum peak, the relative intensity of

the maximum peak, the ratio of the intensity at 600 nm to the intensity of the maximum peak, and the half-value width of a group of peaks are shown in Table 2. This reveals that white light emission is obtained in which a red component sufficiently exists, the spectrum width is very wide, and color rendering properties are high.

#### Comparative Example A-4

A phosphor  $Ba_{0.72}Ca_{1.08}Eu_{0.2}SiO_4$  was produced in the same manner as in Example A-1 with the exception that an aqueous solution of  $Ba(NO_3)_2$ , an aqueous solution of  $Ca(NO_3)_2 \cdot 4H_2O$ , an aqueous solution of  $Eu(NO_3)_3 \cdot 6H_2O$  and a suspension of colloidal silica ( $SiO_2$ ) (the molar ratio of  $Ba(NO_3)_2$ ,  $Ca(NO_3)_2 \cdot 4H_2O$ ,  $Eu(NO_3)_3 \cdot 6H_2O$  and  $SiO_2$  is 0.72:1.08:0.2:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The x and y values of chromaticity coordinates, the wavelength of the maximum peak, the relative intensity of the maximum peak, the ratio of the intensity at 600 nm to the intensity of the maximum peak, and the half-value width of a group of peaks are shown in Table 2. This reveals that when Mn is not added in the composition of Example A-5, no white spectrum is obtained.

#### Comparative Example A-5

A phosphor  $Ba_{1.7}Eu_{0.2}Mn_{0.1}SiO_4$  was produced in the same manner as in Example A-1 with the exception that an aqueous solution of  $Ba(NO_3)_2$ , an aqueous solution of  $Eu(NO_3)_3 \cdot 6H_2O$ , an aqueous solution of  $Mn(NO_3)_2 \cdot 6H_2O$  and a suspension of colloidal silica ( $SiO_2$ ) (the molar ratio of  $Ba(NO_3)_2$ ,  $Eu(NO_3)_3 \cdot 6H_2O$ ,  $Mn(NO_3)_2 \cdot 6H_2O$  and  $SiO_2$  is 1.7:0.2:0.1:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The x and y values of chromaticity coordinates, the wavelength of the maximum peak, the relative intensity of the maximum peak, the ratio of the intensity at 600 nm to the intensity of the maximum peak, and the half-value width of a group of peaks are shown in Table 2. This reveals that when Ca is not added in the composition of Example A-5, no white spectrum is obtained.

#### Comparative Example A-6

A phosphor  $Ca_{1.7}Eu_{0.2}Mn_{0.1}SiO_4$  was produced in the same manner as in Example A-1 with the exception that an aqueous solution of  $Ca(NO_3)_2 \cdot 4H_2O$ , an aqueous solution of  $Eu(NO_3)_3 \cdot 6H_2O$ , an aqueous solution of  $Mn(NO_3)_2 \cdot 6H_2O$  and a suspension of colloidal silica ( $SiO_2$ ) (the molar ratio of  $Ca(NO_3)_2 \cdot 4H_2O$ ,  $Eu(NO_3)_3 \cdot 6H_2O$ ,  $Mn(NO_3)_2 \cdot 6H_2O$  and  $SiO_2$  is 1.7:0.2:0.1:1) were used as original solutions. An emission spectrum at the time when

this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The x and y values of chromaticity coordinates, the wavelength of the maximum peak, the relative intensity of the maximum peak, the ratio of the intensity at 600 nm to the intensity of the maximum peak, and the half-value width of a group of peaks are shown in Table 2. This reveals that when Ba is not added in the composition of Example A-5, no white spectrum is obtained.

#### Example A-6

A phosphor  $\text{Ba}_{0.93}\text{Ca}_{0.62}\text{Eu}_{0.3}\text{Mn}_{0.15}\text{SiO}_4$  was produced in the same manner as in Example A-1 with the exception that an aqueous solution of  $\text{Ba}(\text{NO}_3)_2$ , an aqueous solution of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , an aqueous solution of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , an aqueous solution of  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and a suspension of colloidal silica ( $\text{SiO}_2$ ) (the molar ratio of  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{SiO}_2$  is 0.93:0.62:0.3:0.15:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The x and y values of chromaticity coordinates, the wavelength of the maximum peak, the relative intensity of the maximum peak, the ratio of the intensity at 600 nm to the intensity of the maximum peak, and the half-value width of a

group of peaks are shown in Table 2. This reveals that white light emission is obtained in which a red component sufficiently exists, the spectrum width is very wide, and color rendering properties are high.

#### Example A-7

A phosphor  $\text{Ba}_{1.133}\text{Ca}_{0.378}\text{Zn}_{0.189}\text{Eu}_{0.2}\text{Mn}_{0.1}\text{SiO}_4$  was produced in the same manner as in Example A-1 with the exception that an aqueous solution of  $\text{Ba}(\text{NO}_3)_2$ , an aqueous solution of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , an aqueous solution of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , an aqueous solution of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , an aqueous solution of  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and a suspension of colloidal silica ( $\text{SiO}_2$ ) (the molar ratio of  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{SiO}_2$  is 1.133:0.378:0.189:0.2:0.1:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The x and y values of chromaticity coordinates, the wavelength of the maximum peak, the relative intensity of the maximum peak, the ratio of the intensity at 600 nm to the intensity of the maximum peak, and the half-value width of a group of peaks are shown in Table 2. This reveals that white light emission is obtained in which a red component sufficiently exists, the spectrum width is very wide, and color rendering properties are high.

Table 2

Example or Comparative Example	Chemical Composition of Phosphor	Chromaticity Coordinates		Wavelength of Maximum Peak (nm)	Relative Intensity of Maximum Peak	Intensity at 600 nm/ Intensity of Maximum Peak	Half-Value Width of Group of Peaks (nm)	Molar Ratio of Mn	Ratio of Ca to the Sum of Ba and Ca (molar ratio)
		x	y						
Example A-4	$\text{Ba}_{1.1}\text{Ca}_{0.74}\text{Eu}_{0.06}\text{Mn}_{0.09}\text{SiO}_4$	0.346	0.34	597	157	0.984	208	0.09	0.4
Example A-5	$\text{Ba}_{0.68}\text{Ca}_{1.02}\text{Eu}_{0.2}\text{Mn}_{0.1}\text{SiO}_4$	0.375	0.37	597	115	0.997	194	0.1	0.6
Example A-6	$\text{Ba}_{0.83}\text{Ca}_{0.162}\text{Eu}_{0.3}\text{Mn}_{0.15}\text{SiO}_4$	0.351	0.353	600	89	1	206	0.15	0.4
Example A-7	$\text{Ba}_{1.13}\text{Ca}_{0.376}\text{Zn}_{0.189}\text{Eu}_{0.2}\text{Mn}_{0.1}\text{SiO}_4$	0.363	0.37	598	60	1	193	0.1	0.25
Comparative Example A-4	$\text{Ba}_{0.72}\text{Ca}_{1.08}\text{Eu}_{0.2}\text{SiO}_4$	0.19	0.229	448	110	0.12	104	0	0.6
Comparative Example A-5	$\text{Ba}_{1.7}\text{Eu}_{0.2}\text{Mn}_{0.1}\text{SiO}_4$	0.167	0.527	504	100	0.042	63	0.1	0
Comparative Example A-6	$\text{Ca}_{1.7}\text{Eu}_{0.2}\text{Mn}_{0.1}\text{SiO}_4$	0.254	0.421	504	42	0.27	92	0.1	1

**Example A-8**

$\text{BaCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{Eu}_2\text{O}_3$ ,  $\text{MnCO}_3\cdot\text{nH}_2\text{O}$  and  $\text{SiO}_2$  were weighed to a molar ratio of 1.08:0.72:0.075:0.05:1, and  $\text{NH}_4\text{Cl}$  was added as a flux, followed by mixing in a ball mill for 1 hour. This prepared powder was put in an alumina crucible, further put together with this crucible in a crucible made of carbon, and heated under a stream of nitrogen gas containing 4% of hydrogen at 1200°C for 6 hours, thereby producing a phosphor  $\text{Ba}_{1.08}\text{Ca}_{0.72}\text{Eu}_{0.15}\text{Mn}_{0.05}\text{SiO}_4$ . X-ray diffraction measurement of this phosphor was made under the following conditions. Powder X-ray diffraction measurement was performed using a Bragg-Brentano type powder X-ray diffractometer comprising  $\text{CuK}\alpha$  as an X-ray source which was optically adjusted to  $\Delta 2\theta=0.05^\circ$  or less in the diffraction angle error in a scanning range, under conditions in which the angle reproducibility was assured in which the error of the diffraction angle associated with sample eccentricity is  $\Delta 2\theta=0.05^\circ$  or less using the 111 peak of standard silicon. Further, the divergence angle of a divergence slit was adjusted so that the irradiation width of the X-ray did not exceed the width of the sample in measurement, and for the diffraction peak position (peak top) and diffraction intensity (height), values of the results of measurement in a stationary slit mode was read. The results of X-ray diffraction measurement are shown in Fig. 7. Table 3 shows that the obtained phosphor meets the conditions

described in claim 6, and it was confirmed that the specified phase described above was contained. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, is shown in Fig. 8. In order to remove the influence of an excitation light source on the emission spectrum, light of 420 nm or less was cut. The x and y values of chromaticity coordinates, wavelength of emission peak and intensity of emission peak of this phosphor are shown in Table 4.

#### Example A-9

A phosphor  $Ba_{1.35}Ca_{0.45}Eu_{0.15}Mn_{0.05}SiO_4$  was obtained in the same manner as in Example A-8 with the exception that  $BaCO_3$ ,  $CaCO_3$ ,  $Eu_2O_3$ ,  $MnCO_3 \cdot nH_2O$  and  $SiO_2$  were weighed to a molar ratio of 1.35:0.45:0.075:0.05:1. The results of X-ray diffraction measurement are shown in Table 3, and this example meets the conditions of claim 6. An emission spectrum is shown in Fig. 8, and characteristics are summarized in Table 4.

#### Example A-10

A phosphor  $Ba_{1.20}Ca_{0.4}Sr_{0.2}Eu_{0.15}Mn_{0.05}SiO_4$  was obtained in the same manner as in Example A-8 with the exception that  $BaCO_3$ ,  $CaCO_3$ ,  $SrCO_3$ ,  $Eu_2O_3$ ,  $MnCO_3 \cdot nH_2O$  and  $SiO_2$  were weighed to a molar ratio of 1.20:0.4:0.2:0.075:0.05:1. The results of X-ray

diffraction measurement are shown in Table 3, and this example meets the conditions of claim 6. An emission spectrum is shown in Fig. 8, and characteristics are summarized in Table 4.

#### Example A-11

A phosphor  $Ba_{1.08}Ca_{0.36}Sr_{0.36}Eu_{0.15}Mn_{0.05}SiO_4$  was obtained in the same manner as in Example A-8 with the exception that  $BaCO_3$ ,  $CaCO_3$ ,  $SrCO_3$ ,  $Eu_2O_3$ ,  $MnCO_3 \cdot nH_2O$  and  $SiO_2$  were weighed to a molar ratio of 1.08:0.36:0.36:0.075:0.05:1. The results of X-ray diffraction measurement are shown in Table 3, and this example meets the conditions of claim 6. An emission spectrum is shown in Fig. 8, and characteristics are summarized in Table 4.

Table 3

Example A-8

Reference Diffraction Peak Angle	Angle Range	Start Angle	End Angle	Measured Angle	Measured Relative Intensity
21.366	R1	29.537	30.148	30.061	78.1
Intensity	R2	30.490	31.122	30.864	100.0
54.5	R3	36.122	36.878	36.562	12.2
	R4	37.432	38.217	37.914	25.6
	R5	43.071	43.986	43.712	31.8

Example A-9

Reference Diffraction Peak Angle	Angle Range	Start Angle	End Angle	Measured Angle	Measured Relative Intensity
21.553	R1	29.799	30.415	30.227	73.7
Intensity	R2	30.761	31.398	31.085	100.0
49.4	R3	36.446	37.209	36.666	17.6
	R4	37.767	38.560	38.130	26.6
	R5	43.463	44.387	43.857	28.4

Example A-10

Reference Diffraction Peak Angle	Angle Range	Start Angle	End Angle	Measured Angle	Measured Relative Intensity
21.614	R1	29.884	30.502	30.331	93.0
Intensity	R2	30.849	31.488	31.173	100.0
51.3	R3	36.551	37.317	36.856	13.2
	R4	37.877	38.672	38.248	31.7
	R5	43.590	44.518	44.035	38.4

Example A-11

Reference Diffraction Peak Angle	Angle Range	Start Angle	End Angle	Measured Angle	Measured Relative Intensity
21.702	R1	30.007	30.628	30.448	100.0
Intensity	R2	30.976	31.618	31.262	96.7
42.7	R3	36.512	37.276	37.243	16.3
	R4	38.035	38.834	38.381	29.4
	R5	43.775	44.706	44.197	32.2

Table 4

Example	Chemical Composition of Phosphor	Chromaticity Coordinates		Wavelength of Emission Peak (nm)	Intensity of Emission Peak (arbitrary scale)
		x	y		
Example A-8	$Ba_{1.08}Ca_{0.72}Eu_{0.15}Mn_{0.05}SiO_4$	0.461	0.414	605	113
Example A-9	$Ba_{1.35}Ca_{0.45}Eu_{0.15}Mn_{0.05}SiO_4$	0.537	0.389	601	251
Example A-10	$Ba_{1.20}Ca_{0.4}Sr_{0.2}Eu_{0.15}Mn_{0.05}SiO_4$	0.538	0.415	605	175
Example A-11	$Ba_{1.08}Ca_{0.36}Sr_{0.36}Eu_{0.15}Mn_{0.05}SiO_4$	0.541	0.427	613	113

## Example B-1

An aqueous solution of  $Ba(NO_3)_2$ , an aqueous solution of  $Ca(NO_3)_2 \cdot 4H_2O$ , an aqueous solution of  $Mg(NO_3)_2 \cdot 6H_2O$ , an aqueous solution of  $Eu(NO_3)_3 \cdot 6H_2O$ , an aqueous solution of  $Mn(NO_3)_2 \cdot 6H_2O$  and a suspension of colloidal silica ( $SiO_2$ ) (the molar ratio of  $Ba(NO_3)_2$ ,  $Ca(NO_3)_2 \cdot 4H_2O$ ,  $Mg(NO_3)_2 \cdot 6H_2O$ ,  $Eu(NO_3)_3 \cdot 6H_2O$ ,  $Mn(NO_3)_2 \cdot 6H_2O$  and  $SiO_2$  is 1.133:0.378:0.189:0.2:0.1:1) were mixed in a platinum container and dried. Then, the mixture was burnt by heating under a stream of nitrogen gas containing 4% of hydrogen at  $1050^\circ C$  for 2 hours to produce a phosphor  $Ba_{1.133}Ca_{0.378}Mg_{0.189}Eu_{0.2}Mn_{0.1}SiO_4$  (phosphor used in a second light emitter). An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The wavelength of an emission peak thereof, the intensity of the emission peak at the time when the intensity of an emission peak of Comparative Example B-3 described later is taken as

100 (hereinafter referred to as the relative intensity), and the half-value width are shown in Table 5. This phosphor has a sufficiently wide half-value width, gives good color rendering properties, and emits a light red color having a peak wavelength within the range of 590 nm to 620 nm. This reveals that this phosphor emits reddish light which feels bright.

#### Comparative Example B-1

A phosphor  $\text{Ba}_{1.2}\text{Ca}_{0.4}\text{Mg}_{0.2}\text{Eu}_{0.2}\text{SiO}_4$  was produced in the same manner as in Example B-1 with the exception that an aqueous solution of  $\text{Ba}(\text{NO}_3)_2$ , an aqueous solution of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , an aqueous solution of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , an aqueous solution of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and a suspension of colloidal silica ( $\text{SiO}_2$ ) (the molar ratio of  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{SiO}_2$  is 1.2:0.4:0.2:0.2:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The wavelength, relative intensity and half-value width of an emission peak thereof are shown in Table 5. This shows that when Mn is not added in the composition of Example B-1, no red peak appears.

#### Comparative Example B-2

A phosphor  $\text{Ba}_{0.72}\text{Ca}_{1.08}\text{Eu}_{0.2}\text{SiO}_4$  was produced in the same

manner as in Example B-1 with the exception that an aqueous solution of  $\text{Ba}(\text{NO}_3)_2$ , an aqueous solution of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , an aqueous solution of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and a suspension of colloidal silica ( $\text{SiO}_2$ ) (the molar ratio of  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{SiO}_2$  is 0.72:1.08:0.2:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The wavelength, relative intensity and half-value width of an emission peak thereof are shown in Table 5. This shows that no red peak appears in crystals containing no Mn component or no Mg component.

#### Comparative Example B-3

A phosphor  $\text{Ba}_{1.6}\text{Eu}_{0.2}\text{Mn}_{0.2}\text{SiO}_4$  was produced in the same manner as in Example B-1 with the exception that an aqueous solution of  $\text{Ba}(\text{NO}_3)_2$ , an aqueous solution of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , an aqueous solution of  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and a suspension of colloidal silica ( $\text{SiO}_2$ ) (the molar ratio of  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{SiO}_2$  is 1.6:0.2:0.2:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The wavelength, relative intensity and half-value width of an emission peak thereof are shown in Table 5. This shows that

even though Mn is contained in crystals, when Ca or Mg is not contained, no red peak appears.

#### Comparative Example B-4

A phosphor  $\text{Ca}_{1.6}\text{Eu}_{0.2}\text{Mn}_{0.2}\text{SiO}_4$  was produced in the same manner as in Example B-1 with the exception that an aqueous solution of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , an aqueous solution of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , an aqueous solution of  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and a suspension of colloidal silica ( $\text{SiO}_2$ ) (the molar ratio of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{SiO}_2$  is 1.6:0.2:0.2:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The wavelength, relative intensity and half-value width of an emission peak thereof are shown in Table 5. This shows that even though Mn is contained in crystals, when Ba or Mg is not contained, no red peak appears.

#### Comparative Example B-5

A phosphor  $\text{Ba}_{0.587}\text{Mg}_{1.173}\text{Eu}_{0.2}\text{Mn}_{0.04}\text{SiO}_4$  was produced in the same manner as in Example B-1 with the exception that an aqueous solution of  $\text{Ba}(\text{NO}_3)_2$ , an aqueous solution of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , an aqueous solution of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , an aqueous solution of  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and a suspension of colloidal silica ( $\text{SiO}_2$ ) (the molar ratio of  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,

$\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{SiO}_2$  is 0.587:1.173:0.2:0.04:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The wavelength, relative intensity and half-value width of an emission peak thereof are shown in Table 5. This shows that when Ca does not exist in an adequate amount based on Ba in crystals, the wavelength of emission peak exceeds 620 nm to cause failure to emit reddish light which feels bright.

Table 5

Example or Comparative Example	Chemical Composition of Phosphor	Wavelength of Emission Peak (nm)	Relative Intensity of Emission Peak	Half-Value Width of Emission Peak (nm)	Molar Ratio of Mn	Ratio of Mg to the Sum of Divalent Element Except Eu and Mn, Monovalent, Trivalent and Pentavalent Elements (molar ratio)	Ratio of Ca to the Sum of Ba and Ca (molar ratio)
Example B-1	$\text{Ba}_{1.13}\text{Ca}_{0.37}\text{Mg}_{0.189}\text{Eu}_{0.2}\text{Mn}_{0.1}\text{SiO}_4$	602	147	73	0.1	0.11	0.25
Comparative Example B-1	$\text{Ba}_{1.2}\text{Ca}_{0.4}\text{Mg}_{0.2}\text{Eu}_{0.2}\text{SiO}_4$	496	183	122	0	0.11	0.25
Comparative Example B-2	$\text{Ba}_{0.72}\text{Ca}_{1.08}\text{Eu}_{0.2}\text{SiO}_4$	448	99	104	0	0	0.60
Comparative Example B-3	$\text{Ba}_{1.6}\text{Eu}_{0.1}\text{Mn}_{0.2}\text{SiO}_4$	509	100	62	0.2	0	0.00
Comparative Example B-4	$\text{Ca}_{1.6}\text{Eu}_{0.2}\text{Mn}_{0.2}\text{SiO}_4$	512	25	85	0.2	0	1.00
Comparative Example B-5	$\text{Ba}_{0.887}\text{Mg}_{1.173}\text{Eu}_{0.2}\text{Mn}_{0.04}\text{SiO}_4$	630	94	74	0.04	0.67	0.00

**Example B-2**

A phosphor  $Ba_{1.173}Ca_{0.391}Mg_{0.196}Eu_{0.2}Mn_{0.04}SiO_4$  was produced in the same manner as in Example B-1 with the exception that an aqueous solution of  $Ba(NO_3)_2$ , an aqueous solution of  $Ca(NO_3)_2 \cdot 4H_2O$ , an aqueous solution of  $Mg(NO_3)_2 \cdot 6H_2O$ , an aqueous solution of  $Eu(NO_3)_3 \cdot 6H_2O$ , an aqueous solution of  $Mn(NO_3)_2 \cdot 6H_2O$  and a suspension of colloidal silica ( $SiO_2$ ) (the molar ratio of  $Ba(NO_3)_2$ ,  $Ca(NO_3)_2 \cdot 4H_2O$ ,  $Mg(NO_3)_2 \cdot 6H_2O$ ,  $Eu(NO_3)_3 \cdot 6H_2O$ ,  $Mn(NO_3)_2 \cdot 6H_2O$  and  $SiO_2$  is 1.173:0.391:0.196:0.2:0.04:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. An emission spectrum thereof is shown in Fig. 9. The x and y values of chromaticity coordinates indicating colors, the wavelength of the maximum peak, the intensity of the maximum peak of this phosphor at the time when the intensity of the maximum peak of a phosphor in Comparative Example B-7 described later is taken as 100 (hereinafter referred to as the relative intensity of the maximum peak), the ratio of the intensity at 600 nm to the intensity of the maximum peak, which gives an indication of to what extent a red component exists, and the half-value width of a group of peaks are shown in Table 6. This reveals that white light emission is obtained in which blue, green and red components all sufficiently exist, the spectrum width is very wide, and

color rendering properties are high.

The maximum peak means a peak which is highest in intensity when a plurality of peaks exist in an emission spectrum, and in the case of a single peak, the maximum peak means itself. Further, the half-value width of a group of peaks gives an indication of how wide an emission spectrum distributes, and how high color rendering properties are, and is defined as the total of widths of wavelength regions having an intensity of half or more the intensity of the maximum peak in the spectrum, as shown in Fig. 6.

#### Comparative Example B-6

A phosphor  $Ba_{1.2}Ca_{0.4}Mg_{0.2}Eu_{0.2}SiO_4$  was produced in the same manner as in Example B-1 with the exception that an aqueous solution of  $Ba(NO_3)_2$ , an aqueous solution of  $Ca(NO_3)_2 \cdot 4H_2O$ , an aqueous solution of  $Mg(NO_3)_2 \cdot 6H_2O$ , an aqueous solution of  $Eu(NO_3)_3 \cdot 6H_2O$  and a suspension of colloidal silica ( $SiO_2$ ) (the molar ratio of  $Ba(NO_3)_2$ ,  $Ca(NO_3)_2 \cdot 4H_2O$ ,  $Mg(NO_3)_2 \cdot 6H_2O$ ,  $Eu(NO_3)_3 \cdot 6H_2O$  and  $SiO_2$  is 1.2:0.4:0.2:0.2:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The x and y values of chromaticity coordinates, the wavelength of the maximum peak, the intensity of the maximum peak, the ratio of the intensity at 600 nm to the intensity

of the maximum peak, and the half-value width of a group of peaks are shown in Table 6. This reveals that when Mn is not added in the composition of Example B-5, no white spectrum is obtained.

#### Comparative Example B-7

A phosphor  $Ba_{0.72}Ca_{1.08}Eu_{0.2}SiO_4$  was produced in the same manner as in Example B-1 with the exception that an aqueous solution of  $Ba(NO_3)_2$ , an aqueous solution of  $Ca(NO_3)_2 \cdot 4H_2O$ , an aqueous solution of  $Eu(NO_3)_3 \cdot 6H_2O$  and a suspension of colloidal silica ( $SiO_2$ ) (the molar ratio of  $Ba(NO_3)_2$ ,  $Ca(NO_3)_2 \cdot 4H_2O$ ,  $Eu(NO_3)_3 \cdot 6H_2O$  and  $SiO_2$  is 0.72:1.08:0.2:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The x and y values of chromaticity coordinates, the wavelength of the maximum peak, the intensity of the maximum peak, the ratio of the intensity at 600 nm to the intensity of the maximum peak, and the half-value width of a group of peaks are shown in Table 6. This reveals that when Mn or Mg does not exist in crystals, no white spectrum is obtained.

#### Comparative Example B-8

A phosphor  $Ba_{0.587}Mg_{1.173}Eu_{0.2}Mn_{0.04}SiO_4$  was produced in the same manner as in Example B-1 with the exception that an aqueous

solution of  $\text{Ba}(\text{NO}_3)_2$ , an aqueous solution of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , an aqueous solution of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , an aqueous solution of  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and a suspension of colloidal silica ( $\text{SiO}_2$ ) (the molar ratio of  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{SiO}_2$  is 0.587:1.173:0.2:0.04:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The x and y values of chromaticity coordinates, the wavelength of the maximum peak, the intensity of the maximum peak, the ratio of the intensity at 600 nm to the intensity of the maximum peak, and the half-value width of a group of peaks are shown in Table 6. When Ca does not exist in an adequate amount based on Ba in crystals, the wavelength of a red peak exceeds 620 nm to obtain a visible light spectrum containing no reddish component which feels bright.

Table 6

Example or Comparative Example	Chemical Composition of Phosphor	Chromaticity Coordinates		Wavelength of Maximum Peak (nm)	Relative Intensity of Maximum Peak	Intensity at 600 nm/ Intensity of Maximum Peak	Half-Value Width of Group of Peaks (nm)	Molar Ratio of Mn	Ratio of Mg to the Sum of Divalent Element Except Eu and Mn, Monovalent, Trivalent and Pentavalent Elements (molar ratio)	Ratio of Ca to the Sum of Ba and Ca (molar ratio)
		x	y							
Example B-2	$Ba_{1.773}Ca_{0.331}Mg_{0.195}Eu_{0.2}Mn_{0.04}SiO_4$	0.376	0.345	598	202	1	158	0.04	0.11	0.25
Comparative Example B-6	$Ba_{1.2}Ca_{0.4}Mg_{0.2}Eu_{0.2}SiO_4$	0.184	0.29	496	186	0.08	122	0	0.11	0.25
Comparative Example B-7	$Ba_{1.72}Ca_{1.08}Eu_{0.2}SiO_4$	0.19	0.229	448	100	0.12	104	0	0	0.60
Comparative Example B-8	$Ba_{0.587}Mg_{1.173}Eu_{0.2}Mn_{0.04}SiO_4$	0.455	0.291	630	96	0.56	74	0.04	0.67	0.00

## Example B-3

$\text{BaCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{Eu}_2\text{O}_3$ ,  $\text{MnCO}_3\cdot\text{nH}_2\text{O}$  and  $\text{SiO}_2$  were weighed to a molar ratio of 1.283:0.428:0.09:0.075:0.05:1, and  $\text{NH}_4\text{Cl}$  was added as a flux, followed by mixing in a ball mill for 1 hour. This prepared powder was put in an alumina crucible, further put together with this crucible in a crucible made of carbon, and heated under a stream of nitrogen gas containing 4% of hydrogen at  $1200^\circ\text{C}$  for 6 hours, thereby producing a phosphor  $\text{Ba}_{1.283}\text{Ca}_{0.428}\text{Mg}_{0.09}\text{Eu}_{0.15}\text{Mn}_{0.05}\text{SiO}_4$ . X-ray diffraction measurement of this phosphor was made under the following conditions. Powder X-ray diffraction measurement was performed using a Bragg-Brentano type powder X-ray diffractometer comprising  $\text{CuK}\alpha$  as an X-ray source which was optically adjusted to  $\Delta 2\theta=0.05^\circ$  or less in the diffraction angle error in a scanning range, under conditions in which the angle reproducibility was assured in which the error of the diffraction angle associated with sample eccentricity is  $\Delta 2\theta=0.05^\circ$  or less using the 111 peak of standard silicon. Further, the divergence angle of a divergence slit was adjusted so that the irradiation width of the X-ray did not exceed the width of the sample in measurement, and for the diffraction peak position (peak top) and diffraction intensity (height), values of the results of measurement in a stationary slit mode was read. The results of X-ray diffraction measurement are shown in Fig. 10. Table 7 shows that the obtained phosphor

meets the conditions described in claim 6, and it was confirmed that the specified phase described above was contained. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, is shown in Fig. 11. In order to remove the influence of an excitation light source on the emission spectrum, light of 420 nm or less was cut. The x and y values of chromaticity coordinates, wavelength of emission peak and intensity of emission peak of this phosphor are shown in Table 8.

#### Example B-4

A phosphor  $Ba_{1.215}Ca_{0.405}Mg_{0.18}Eu_{0.15}Mn_{0.05}SiO_4$  was obtained in the same manner as in Example B-3 with the exception that  $BaCO_3$ ,  $CaCO_3$ ,  $MgCO_3$ ,  $Eu_2O_3$ ,  $MnCO_3 \cdot nH_2O$  and  $SiO_2$  were weighed to a molar ratio of 1.215:0.405:0.180:0.075:0.05:1. The results of X-ray diffraction measurement are shown in Table 7, and this example meets the conditions of claim 6. An emission spectrum is shown in Fig. 11, and characteristics are summarized in Table 8.

#### Example B-5

A phosphor  $Ba_{0.855}Ca_{0.285}Sr_{0.57}Mg_{0.09}Eu_{0.15}Mn_{0.05}SiO_4$  was obtained in the same manner as in Example B-3 with the exception that  $BaCO_3$ ,  $CaCO_3$ ,  $SrCO_3$ ,  $MgCO_3$ ,  $Eu_2O_3$ ,  $MnCO_3 \cdot nH_2O$  and  $SiO_2$  were

weighed to a molar ratio of 0.855:0.285:0.57:0.09:0.075:0.05:1. The results of X-ray diffraction measurement are shown in Table 7, and this example meets the conditions of claim 6. An emission spectrum is shown in Fig. 11, and characteristics are summarized in Table 8.

#### Example B-6

A phosphor  $Ba_{0.81}Ca_{0.27}Sr_{0.54}Mg_{0.18}Eu_{0.15}Mn_{0.05}SiO_4$  was obtained in the same manner as in Example B-3 with the exception that  $BaCO_3$ ,  $CaCO_3$ ,  $SrCO_3$ ,  $MgCO_3$ ,  $Eu_2O_3$ ,  $MnCO_3 \cdot nH_2O$  and  $SiO_2$  were weighed to a molar ratio of 0.810:0.27:0.54:0.18:0.075:0.05:1. The results of X-ray diffraction measurement are shown in Table 7, and this example does not meet the conditions of claim 6. An emission spectrum is shown in Fig. 11, and characteristics are summarized in Table 8.

Table 7

Example B-3

Reference Diffraction Peak Angle	Angle Range	Start Angle	End Angle	Measured Angle	Measured Relative Intensity
21.512	R1	29.741	30.356	30.222	88.0
Intensity	R2	30.701	31.337	31.108	100.0
67.5	R3	36.375	37.136	36.723	17.0
	R4	37.694	38.485	38.207	35.9
	R5	43.377	44.299	44.006	43.6

Example B-4

Reference Diffraction Peak Angle	Angle Range	Start Angle	End Angle	Measured Angle	Measured Relative Intensity
21.761	R1	30.089	30.712	30.523	94.0
Intensity	R2	31.061	31.705	31.396	100.0
70.1	R3	36.806	37.577	37.049	18.7
	R4	38.141	38.943	38.528	32.4
	R5	43.898	44.833	44.346	41.1

Example B-5

Reference Diffraction Peak Angle	Angle Range	Start Angle	End Angle	Measured Angle	Measured Relative Intensity
21.834	R1	30.191	30.816	30.641	72.8
Intensity	R2	31.167	31.813	31.572	100.0
27.5	R3	36.932	37.706	37.508	23.0
	R4	38.273	39.077	38.618	24.9
	R5	44.052	44.990	44.479	22.2

Example B-6

Reference Diffraction Peak Angle	Angle Range	Start Angle	End Angle	Measured Angle	Measured Relative Intensity
21.764	R1	30.094	30.716	30.568	56.3
Intensity	R2	31.066	31.710	31.500	100.0
19.2	R3	36.811	37.582	37.433	16.2
	R4	38.147	38.948	38.544	19.1
	R5	43.905	44.839	44.405	15.8

Table 8

Example	Chemical Composition of Phosphor	Chromaticity Coordinates		Wavelength of Emission Peak (nm)	Intensity of Emission Peak (arbitrary scale)
		x	y		
Example B-3	$Ba_{1.283}Ca_{0.428}Mg_{0.09}Eu_{0.15}Mn_{0.05}SiO_4$	0.510	0.373	612	439
Example B-4	$Ba_{1.215}Ca_{0.405}Mg_{0.18}Eu_{0.15}Mn_{0.05}SiO_4$	0.491	0.364	622	404
Example B-5	$Ba_{0.855}Ca_{0.285}Sr_{0.57}Mg_{0.09}Eu_{0.15}Mn_{0.05}SiO_4$	0.528	0.429	623	143
Example B-6	$Ba_{0.81}Ca_{0.27}Sr_{0.54}Mg_{0.18}Eu_{0.15}Mn_{0.05}SiO_4$	0.499	0.421	629	100

## Example C-1

An aqueous solution of  $Ba(NO_3)_2$ , an aqueous solution of  $Mg(NO_3)_2 \cdot 6H_2O$ , an aqueous solution of  $Eu(NO_3)_3 \cdot 6H_2O$ , an aqueous solution of  $Mn(NO_3)_2 \cdot 6H_2O$  and a suspension of colloidal silica ( $SiO_2$ ) (the molar ratio of  $Ba(NO_3)_2$ ,  $Mg(NO_3)_2 \cdot 6H_2O$ ,  $Eu(NO_3)_3 \cdot 6H_2O$ ,  $Mn(NO_3)_2 \cdot 6H_2O$  and  $SiO_2$  is 0.935:0.935:0.1:0.03:1) were mixed in a platinum container and dried. Then, the mixture was burnt by heating under a stream of nitrogen gas containing 4% of hydrogen at 1050°C for 2 hours to produce a phosphor  $Ba_{0.935}Mg_{0.935}Eu_{0.1}Mn_{0.03}SiO_4$  (phosphor used in a second light emitter). An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The wavelength of an emission peak thereof, the intensity of the emission peak at the time when the intensity of an emission peak of Comparative Example C-5 described later is taken as 100 (hereinafter referred to as the relative intensity), and

the half-value width are shown in Table 9. This reveals that this phosphor emits strong red light giving high color rendering properties because of its sufficiently high intensity and wide half-value width, and that it emits bright deep red light, because the wavelength of emission peak is in the region of 615 nm to 645 nm. According to measurement of an excitation spectrum at a peak wavelength of 630 nm in excitation at 400 nm, relative intensities at excitation wavelengths of 254 nm, 280 nm, 382 nm and 400 nm are 208, 328, 351 and 320, respectively, and light emission by excitation at around 400 nm is strong 1.5 times or more the conventional light emission by excitation at 254 nm. This shows that this phosphor is a phosphor which is very advantageous to a light source of a GaN-based semiconductor.

#### Comparative Example C-1

A phosphor  $Ba_{0.95}Mg_{0.95}Eu_{0.1}SiO_4$  was produced in the same manner as in Example C-1 with the exception that an aqueous solution of  $Ba(NO_3)_2$ , an aqueous solution of  $Mg(NO_3)_2 \cdot 6H_2O$ , an aqueous solution of  $Eu(NO_3)_3 \cdot 6H_2O$  and a suspension of colloidal silica ( $SiO_2$ ) (the molar ratio of  $Ba(NO_3)_2$ ,  $Mg(NO_3)_2 \cdot 6H_2O$ ,  $Eu(NO_3)_3 \cdot 6H_2O$  and  $SiO_2$  is 0.95:0.95:0.1:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The

wavelength, relative intensity and half-value width of an emission peak thereof are shown in Table 9. This shows that when Mn is not added in the composition of Example C-1, no red peak appears.

#### Example C-2

A phosphor  $\text{Ba}_{0.623}\text{Mg}_{1.247}\text{Eu}_{0.1}\text{Mn}_{0.03}\text{SiO}_4$  was produced in the same manner as in Example C-1 with the exception that an aqueous solution of  $\text{Ba}(\text{NO}_3)_2$ , an aqueous solution of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , an aqueous solution of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , an aqueous solution of  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and a suspension of colloidal silica ( $\text{SiO}_2$ ) (the molar ratio of  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{SiO}_2$  is 0.623:1.247:0.1:0.03:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The wavelength, relative intensity and half-value width of an emission peak thereof are shown in Table 9. This reveals that this phosphor emits strong red light giving high color rendering properties because of its sufficiently high intensity and wide half-value width, and that it emits bright deep red light, because the wavelength of emission peak is in the region of 615 nm to 645 nm.

#### Comparative Example C-2

A phosphor  $Ba_{0.633}Mg_{1.267}Eu_{0.1}SiO_4$  was produced in the same manner as in Example C-1 with the exception that an aqueous solution of  $Ba(NO_3)_2$ , an aqueous solution of  $Mg(NO_3)_2 \cdot 6H_2O$ , an aqueous solution of  $Eu(NO_3)_3 \cdot 6H_2O$  and a suspension of colloidal silica ( $SiO_2$ ) (the molar ratio of  $Ba(NO_3)_2$ ,  $Mg(NO_3)_2 \cdot 6H_2O$ ,  $Eu(NO_3)_3 \cdot 6H_2O$  and  $SiO_2$  is 0.633:1.267:0.1:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The wavelength, relative intensity and half-value width of an emission peak thereof are shown in Table 9. This shows that when Mn is not added in the composition of Example C-2, no red peak appears.

### Example C-3

A phosphor  $Ba_{0.587}Mg_{1.173}Eu_{0.2}Mn_{0.04}SiO_4$  was produced in the same manner as in Example C-1 with the exception that an aqueous solution of  $Ba(NO_3)_2$ , an aqueous solution of  $Mg(NO_3)_2 \cdot 6H_2O$ , an aqueous solution of  $Eu(NO_3)_3 \cdot 6H_2O$ , an aqueous solution of  $Mn(NO_3)_2 \cdot 6H_2O$  and a suspension of colloidal silica ( $SiO_2$ ) (the molar ratio of  $Ba(NO_3)_2$ ,  $Mg(NO_3)_2 \cdot 6H_2O$ ,  $Eu(NO_3)_3 \cdot 6H_2O$ ,  $Mn(NO_3)_2 \cdot 6H_2O$  and  $SiO_2$  is 0.587:1.173:0.2:0.04:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode,

was measured. An emission spectrum thereof is shown in Fig. 12. In order to remove the influence of an excitation light source on the emission spectrum, the measurement was made introducing a filter for cutting light of 420 nm or less. The wavelength, relative intensity and half-value width of an emission peak thereof are shown in Table 9. This reveals that this phosphor emits strong red light giving high color rendering properties because of its sufficiently high intensity and wide half-value width, and that it emits bright deep red light, because the wavelength is in the region of 615 nm to 645 nm.

#### Comparative Example C-3

A phosphor  $Ba_{0.6}Mg_{1.2}Eu_{0.2}SiO_4$  was produced in the same manner as in Example C-1 with the exception that an aqueous solution of  $Ba(NO_3)_2$ , an aqueous solution of  $Mg(NO_3)_2 \cdot 6H_2O$ , an aqueous solution of  $Eu(NO_3)_3 \cdot 6H_2O$  and a suspension of colloidal silica ( $SiO_2$ ) (the molar ratio of  $Ba(NO_3)_2$ ,  $Mg(NO_3)_2 \cdot 6H_2O$ ,  $Eu(NO_3)_3 \cdot 6H_2O$  and  $SiO_2$  is 0.6:1.2:0.2:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The wavelength, relative intensity and half-value width of an emission peak thereof are shown in Table 9. This shows that when Mn is not added in the composition of Example C-3, no red

peak appears.

#### Comparative Example C-4

A phosphor  $Ba_{1.7}Eu_{0.2}Mn_{0.1}SiO_4$  was produced in the same manner as in Example C-1 with the exception that an aqueous solution of  $Ba(NO_3)_2$ , an aqueous solution of  $Eu(NO_3)_3 \cdot 6H_2O$ , an aqueous solution of  $Mn(NO_3)_2 \cdot 6H_2O$  and a suspension of colloidal silica ( $SiO_2$ ) (the molar ratio of  $Ba(NO_3)_2$ ,  $Eu(NO_3)_3 \cdot 6H_2O$ ,  $Mn(NO_3)_2$  and  $SiO_2$  is 1.7:0.2:0.1:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The wavelength, relative intensity and half-value width of an emission peak thereof are shown in Table 9. This shows that even though Mn is contained in crystals, when Mg is not contained, no red peak appears.

#### Comparative Example C-5

A phosphor  $Ba_{0.567}Ca_{0.567}Mg_{0.566}Eu_{0.2}Mn_{0.1}SiO_4$  was produced in the same manner as in Example C-1 with the exception that an aqueous solution of  $Ba(NO_3)_2$ , an aqueous solution of  $Ca(NO_3)_2 \cdot 4H_2O$ , an aqueous solution of  $Mg(NO_3)_2 \cdot 6H_2O$ , an aqueous solution of  $Eu(NO_3)_3 \cdot 6H_2O$ , an aqueous solution of  $Mn(NO_3)_2 \cdot 6H_2O$  and a suspension of colloidal silica ( $SiO_2$ ) (the molar ratio of  $Ba(NO_3)_2$ ,  $Ca(NO_3)_2$ ,  $Mg(NO_3)_2 \cdot 6H_2O$ ,  $Eu(NO_3)_3 \cdot 6H_2O$ ,  $Mn(NO_3)_2 \cdot 6H_2O$

and  $\text{SiO}_2$  is 0.567:0.567:0.566:0.2:0.1:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The wavelength, relative intensity and half-value width of an emission peak thereof are shown in Table 9. This shows that when the existing amount of Ca is too much to Ba, the wavelength of emission peak becomes less than 615 nm to cause failure to emit bright deep red light.

Table 9

Example or Comparative Example	Chemical Composition of Phosphor	Wavelength of Emission Peak (nm)	Relative Intensity of Emission Peak	Half-Value Width of Emission Peak (nm)	Molar Ratio of Eu	Molar Ratio of Mn	Ratio of Mg to the Sum of Divalent Element Except Eu and Mn, Monovalent, Trivalent and Pentavalent Elements (molar ratio)	Ratio of Ca to the Sum of Ba and Ca (molar ratio)
Example C-1	$\text{Ba}_{0.935}\text{Mg}_{0.035}\text{Eu}_{0.1}\text{Mn}_{0.03}\text{SiO}_4$	630	320	74	0.1	0.03	0.5	0
Example C-2	$\text{Ba}_{0.622}\text{Mg}_{1.247}\text{Eu}_{0.1}\text{Mn}_{0.03}\text{SiO}_4$	633	191	73	0.1	0.03	0.67	0
Example C-3	$\text{Ba}_{0.58}\text{Mg}_{1.173}\text{Eu}_{0.2}\text{Mn}_{0.04}\text{SiO}_4$	630	127	74	0.2	0.04	0.67	0
Comparative Example C-1	$\text{Ba}_{0.85}\text{Mg}_{0.05}\text{Eu}_{0.1}\text{SiO}_4$	442	246	117	0.1	0	0.5	0
Comparative Example C-2	$\text{Ba}_{0.833}\text{Mg}_{1.267}\text{Eu}_{0.1}\text{SiO}_4$	443	162	97	0.1	0	0.67	0
Comparative Example C-3	$\text{Ba}_{0.8}\text{Mg}_{1.2}\text{Eu}_{0.2}\text{SiO}_4$	438	323	42	0.2	0	0.67	0
Comparative Example C-4	$\text{Ba}_{1.7}\text{Eu}_{0.2}\text{Mn}_{0.1}\text{SiO}_4$	504	122	63	0.2	0.1	0	0
Comparative Example C-5	$\text{Ba}_{0.567}\text{Ca}_{0.433}\text{Mg}_{0.05}\text{Eu}_{0.2}\text{Mn}_{0.1}\text{SiO}_4$	602	100	95	0.2	0.1	0.33	0.5

## Example C-4

A phosphor  $Ba_{0.92}Mg_{0.92}Eu_{0.1}Mn_{0.06}SiO_4$  was produced in the same manner as in Example C-1 with the exception that an aqueous solution of  $Ba(NO_3)_2$ , an aqueous solution of  $Mg(NO_3)_2 \cdot 6H_2O$ , an aqueous solution of  $Eu(NO_3)_3 \cdot 6H_2O$ , an aqueous solution of  $Mn(NO_3)_2 \cdot 6H_2O$  and a suspension of colloidal silica ( $SiO_2$ ) (the molar ratio of  $Ba(NO_3)_2$ ,  $Mg(NO_3)_2 \cdot 6H_2O$ ,  $Eu(NO_3)_3 \cdot 6H_2O$ ,  $Mn(NO_3)_2 \cdot 6H_2O$  and  $SiO_2$  is 0.92:0.92:0.1:0.06:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. An emission spectrum thereof is shown in Fig. 13. The wavelength and relative intensity of a peak of 590 nm or more (a peak of a red component), the wavelength and relative intensity of the maximum peak of less than 590 nm, the half-value width of a group of peaks and the x and y values of chromaticity coordinates indicating colors are shown in Table 10. This shows that a wide spectrum containing a deep red component in which the peak wavelength is in the region of 615 nm to 645 nm and also containing blue and green components is obtained to give high color rendering properties, resulting in bright white light emission.

The maximum peak of less than 590 nm means a peak which is highest in intensity when a plurality of peaks exist in the region of less than 590 nm in an emission spectrum, and in the

case of a single peak, the maximum peak means itself. Further, the half-value width of a group of peaks gives an indication of how wide an emission spectrum distributes, and how high color rendering properties are, and is defined as the total of widths of wavelength regions having an intensity of half or more the intensity of the maximum peak in the spectrum, as shown in Fig. 6.

#### Comparative Example C-6

A phosphor  $Ba_{0.95}Mg_{0.95}Eu_{0.1}SiO_4$  emitting white light was produced in the same manner as in Example C-1 with the exception that an aqueous solution of  $Ba(NO_3)_2$ , an aqueous solution of  $Mg(NO_3)_2 \cdot 6H_2O$ , an aqueous solution of  $Eu(NO_3)_3 \cdot 6H_2O$  and a suspension of colloidal silica ( $SiO_2$ ) (the molar ratio of  $Ba(NO_3)_2$ ,  $Mg(NO_3)_2 \cdot 6H_2O$ ,  $Eu(NO_3)_3 \cdot 6H_2O$  and  $SiO_2$  is 0.95:0.95:0.1:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The wavelength and relative intensity of a peak of a red component, the wavelength and relative intensity of the maximum peak of less than 590 nm, the half-value width of a group of peaks and the x and y values of chromaticity coordinates are shown in Table 10. This shows that when Mn is not added in the composition of Example C-4, no red peak appears.

### Comparative Example C-7

A phosphor  $Ba_{1.2}Ca_{0.2}Mg_{0.4}Eu_{0.2}SiO_4$  was produced in the same manner as in Example C-1 with the exception that an aqueous solution of  $Ba(NO_3)_2$ , an aqueous solution of  $Ca(NO_3)_2 \cdot 4H_2O$ , an aqueous solution of  $Mg(NO_3)_2 \cdot 6H_2O$ , an aqueous solution of  $Eu(NO_3)_3 \cdot 6H_2O$  and a suspension of colloidal silica ( $SiO_2$ ) (the molar ratio of  $Ba(NO_3)_2$ ,  $Ca(NO_3)_2 \cdot 4H_2O$ ,  $Mg(NO_3)_2 \cdot 6H_2O$ ,  $Eu(NO_3)_3 \cdot 6H_2O$  and  $SiO_2$  is 1.2:0.2:0.4:0.2:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The wavelength and relative intensity of a peak of a red component, the wavelength and relative intensity of the maximum peak of less than 590 nm, the half-value width of a group of peaks and the x and y values of chromaticity coordinates are shown in Table 10. This shows that when Mn is not added in the composition of Example C-5, no red peak appears.

### Example C-5

A phosphor  $Ba_{0.82}Mg_{0.82}Eu_{0.3}Mn_{0.06}SiO_4$  was produced in the same manner as in Example C-1 with the exception that an aqueous solution of  $Ba(NO_3)_2$ , an aqueous solution of  $Mg(NO_3)_2 \cdot 6H_2O$ , an aqueous solution of  $Eu(NO_3)_3 \cdot 6H_2O$ , an aqueous solution of

$\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and a suspension of colloidal silica ( $\text{SiO}_2$ ) (the molar ratio of  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{SiO}_2$  is 0.82:0.82:0.3:0.06:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The wavelength and relative intensity of a peak of a red component, the wavelength and relative intensity of the maximum peak of less than 590 nm, the half-value width of a group of peaks and the x and y values of chromaticity coordinates are shown in Table 10. This shows that a wide spectrum containing a deep red component in which the peak wavelength is in the region of 615 nm to 645 nm and also containing blue and green components is obtained to give high color rendering properties, resulting in bright white light emission.

#### Comparative Example C-8

A phosphor  $\text{Ba}_{0.85}\text{Mg}_{0.85}\text{Eu}_{0.3}\text{SiO}_4$  was produced in the same manner as in Example C-1 with the exception that an aqueous solution of  $\text{Ba}(\text{NO}_3)_2$ , an aqueous solution of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , an aqueous solution of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and a suspension of colloidal silica ( $\text{SiO}_2$ ) (the molar ratio of  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{SiO}_2$  is 0.85:0.85:0.3:1) were used as original solutions. An emission spectrum at the time when this phosphor

was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The wavelength and relative intensity of a peak of a red component, the wavelength and relative intensity of the maximum peak of less than 590 nm, the half-value width of a group of peaks and the x and y values of chromaticity coordinates are shown in Table 10. This shows that when Mn is not added in the composition of Example C-6, no red peak appears.

#### Comparative Example C-9

A phosphor  $\text{Ba}_{0.88}\text{Ca}_{0.44}\text{Mg}_{0.44}\text{Eu}_{0.2}\text{Mn}_{0.04}\text{SiO}_4$  was produced in the same manner as in Example C-1 with the exception that an aqueous solution of  $\text{Ba}(\text{NO}_3)_2$ , an aqueous solution of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , an aqueous solution of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , an aqueous solution of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , an aqueous solution of  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and a suspension of colloidal silica ( $\text{SiO}_2$ ) (the molar ratio of  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{SiO}_2$  is 0.88:0.44:0.44:0.2:0.04:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The wavelength and relative intensity of a peak of a red component, the wavelength and relative intensity of the maximum peak of less than 590 nm, the half-value width of a group of peaks and the x and y values of chromaticity coordinates are shown in

Table 10. This shows that when Ca exists in an amount as much as half of Ba in crystals, the peak wavelength of a red component becomes less than 615 nm to cause failure to emit bright white light.

#### Comparative Example C-10

A phosphor  $Ba_{1.144}Ca_{0.216}Mg_{0.48}Eu_{0.01}Mn_{0.15}SiO_4$  was produced in the same manner as in Example C-1 with the exception that an aqueous solution of  $Ba(NO_3)_2$ , an aqueous solution of  $Ca(NO_3)_2 \cdot 4H_2O$ , an aqueous solution of  $Mg(NO_3)_2 \cdot 6H_2O$ , an aqueous solution of  $Eu(NO_3)_3 \cdot 6H_2O$ , an aqueous solution of  $Mn(NO_3)_2 \cdot 6H_2O$  and a suspension of colloidal silica ( $SiO_2$ ) (the molar ratio of  $Ba(NO_3)_2$ ,  $Ca(NO_3)_2$ ,  $Mg(NO_3)_2 \cdot 6H_2O$ ,  $Eu(NO_3)_3 \cdot 6H_2O$ ,  $Mn(NO_3)_2 \cdot 6H_2O$  and  $SiO_2$  is 1.144:0.216:0.48:0.01:0.15:1) were used as original solutions. An emission spectrum at the time when this phosphor was excited at 400 nm, a main wavelength in an ultraviolet light region of a GaN-based light emitting diode, was measured. The wavelength and relative intensity of a peak of a red component, the wavelength and relative intensity of the maximum peak of less than 590 nm, the half-value width of a group of peaks and the x and y values of chromaticity coordinates are shown in Table 10. This shows that when the molar ratio of Eu is as small as 0.01, the intensity of a red component becomes somewhat small.

Table 10

Example or Comparative Example	Chemical Composition of Phosphor	Peak of 590 nm or More (Peak of Red Component)		Maximum Peak of Less Than 590 nm		Chromaticity Coordinates		Molar Ratio of Eu	Molar Ratio of Mn	Ratio of Mg to the Sum of Divalent Element Except Eu and Mn, Monovalent, Trivalent and Pentavalent Elements (molar ratio)
		Wave-length (nm)	Relative Intensity	Wave-length (nm)	Relative Intensity	X	Y			
Example C-4	$\text{Ba}_{0.92}\text{Mg}_{0.02}\text{Eu}_{0.1}\text{Mn}_{0.06}\text{SiO}_4$	629	147	521	76	101	0.384	0.33	0.1	0.06
Example C-5	$\text{Ba}_{0.82}\text{Mg}_{0.08}\text{Eu}_{0.3}\text{Mn}_{0.05}\text{SiO}_4$	637	108	507	72	124	0.373	0.328	0.3	0.06
Comparative Example C-6	$\text{Ba}_{0.75}\text{Mg}_{0.05}\text{Eu}_{1.1}\text{SiO}_4$	-	0	442	246	119	0.167	0.267	0.1	0
Comparative Example C-7	$\text{Ba}_{1.2}\text{Ca}_{0.2}\text{Mg}_{0.4}\text{Eu}_{0.2}\text{SiO}_4$	-	0	509	465	73	0.199	0.476	0.2	0
Comparative Example C-8	$\text{Ba}_{0.85}\text{Mg}_{0.05}\text{Eu}_{0.3}\text{SiO}_4$	-	0	507	227	118	0.180	0.284	0.3	0
Comparative Example C-9	$\text{Ba}_{0.8}\text{Ca}_{0.44}\text{Mg}_{0.44}\text{Eu}_{0.2}\text{Mn}_{0.04}\text{SiO}_4$	600	128	470	100	172	0.356	0.333	0.2	0.04
Comparative Example C-10	$\text{Ba}_{1.14}\text{Ca}_{0.216}\text{Mg}_{0.48}\text{Eu}_{0.01}\text{Mn}_{0.15}\text{SiO}_4$	637	41	429	68	101	0.316	0.177	0.01	0.15
										0.26
										0.16

Although the present invention has been described in detail using particular embodiments, it will be obvious to those skilled in the art that various changes and variations are possible without departing from the spirit and scope of the invention.

The present application is based on Japanese Patent Application (Patent Application No. 2004-9768) filed on January 16, 2004, Patent Application (Patent Application No. 2004-9769) filed on January 16, 2004, and Patent Application (Patent Application No. 2004-9770) filed on January 16, 2004, the whole of which is incorporated herein by reference.

#### Industrial Applicability

According to the present invention, there can be provided a high-efficiency red light emitting phosphor and white phosphor for using in a display or lighting which high-efficiently emits light in combination with a light source which emits light in the region from near-ultraviolet light to visible light.

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